Co-ordination of (*o*-Aminophenyl)diphenylphosphine in Complexes containing the $[\mathrm{M^V{=}O}]^{3+}$ (M = Tc or Re) Core[†]

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Reduction–substitution reactions of $[\mathrm{TcO_4}]^-$ with (*o*-aminophenyl)diphenylphosphine (HL) at a strictly controlled stoichiometric metal/ligand ratio gave neutral oxotechnetium(V) complexes of the type $[\mathrm{TcOL_2(OR)}]$ (R = Me **1** or Et **2**). Analogous $[\mathrm{ReOL_2(OR)}]$ species (R = H **3**, Me **4**, Et **5**, Pr **6**, Bu **7**, C_2H_4OH **8**, C_3H_6OH **9**, Ph **10** or OCMe **11**) are instead produced *via* ligand-exchange reactions in basic media starting from $[\mathrm{ReOCl_4}]^-$. Compounds **1–11** are referred to as 'equatorial' because the co-ordination of both bidentate L^- chelates occurs symmetrically in the equatorial plane orthogonal to the M=O moiety, with a mutual *cis*-phosphorus configuration. The site *trans* to the oxo group is always occupied by an oxygen-containing monodentate ligand the co-ordination of which determines the stability of this class of octahedral complexes. Nevertheless the $^-$OR group is easily exchangeable with other nucleophiles available in the reaction mixture by the mass effect and/or donor ability of the incoming ligand. The crystal structures of complexes **1** and **5** have been determined: **1**, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 12.156(3)$, $b = 26.005(6)$, $c = 10.953(2)$ Å, $\beta = 102.49(2)°$, R' 0.0611 using 1766 observed reflections; Tc–O(1) 1.700(8), Tc–O(2) 1.999(8), Tc–P 2.511(3) and 2.503(4), Tc–N 1.972(10) and 1.976(8) Å; O(1)–Tc–N 105.8(4) and 103.6(4), O(1)–Tc–P 88.1(3) and 88.9(2), O(1)–Tc–O(2) 158.3(3)°; **5**, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 12.056(3)$, $b = 26.303(6)$, $c = 11.005(3)$ Å, $\beta = 102.32(2)°$, R' 0.0614 using 4752 observed reflections; Re–O(1) 1.692(7), Re–O(2) 2.004(7), Re–P 2.495(2) and 2.493(3), Re–N 1.990(8) and 2.003(7) Å; O(1)–Re–N 104.6(3) and 102.6(3), O(1)–Re–P 89.1(2) and 88.8(2), O(1)–Re–O(2) 160.8(3)°. By treatment of $[\mathrm{MOL_2(OR)}]$ solutions with HX (X = halide), further reduction to lower-oxidation-state species occurs when M = Tc, while another class of stable and neutral oxo complexes, termed 'twisted', is produced when M = Re. Two mutually orthogonal L^- chelates co-ordinate the metal while still preserving the *cis*-phosphorus configuration, one ligand bridging an equatorial and an apical position (with the phosphinoamido nitrogen *trans* to the Re=O linkage) and the other two equatorial positions. The equatorial plane is completed by a halide atom. The chloro derivative $[\mathrm{ReOL_2Cl}]$ exhibits two crystalline forms, α (**12**) and β (**13**), the crystal structures of which have been determined: **12**, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 9.594(1)$, $b = 18.565(4)$, $c = 17.656(2)$ Å, $\beta = 91.00(1)°$, R' 0.0477 using 2979 observed reflections; Re–O 1.767(7), Re–Cl 2.436(3), Re–P(1) 2.429(3), Re–P(2) 2.479(3), Re–N(1) 1.986(9), Re–N(2) 2.029(8) Å; O–Re–N(2) 162.8(3), O–Re–N(1) 108.6(3)°; **13**, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 10.196(5)$, $b = 14.047(6)$, $c = 21.987(8)$ Å, R' 0.0671 using 2501 observed reflections; Re–O 1.69(1), Re–Cl 2.422(6), Re–P(1) 2.434(5), Re–P(2) 2.476(5), Re–N(1) 2.01(1), Re–N(2) 2.04(1) Å; O–Re–N(2) 162.7(6), O–Re–N(1) 109.0(7)°. The interconversion between 'equatorial' and 'twisted' species is discussed. Elemental analyses, FAB mass, IR, electronic, ^{1}H and ^{31}P NMR spectra are reported. The ^{31}P NMR signal is diagnostic for both classes of complexes in solution, being a singlet for the 'equatorial' and two doublets for the 'twisted' species, respectively.

As part of a systematic investigation on the chemistry of bidentate functionalized phosphines toward technetium we recently reported on the reactivity of the ligand (*o*-aminophenyl)diphenylphosphine $PPh_2(C_6H_4NH_2\text{-}2)$ (HL) with pertechnetate. Working with a five-fold molar excess of ligand, depending on the pH of the reaction medium, two technetium(III) species were obtained.[1] The compound HL contains a 'hard' anilino group and a tertiary 'soft' phosphorus(III) atom, which can both reduce the pertechnetate anion and act as a neutral or negatively charged co-ordinating ligand. In general, tertiary phosphines stabilize the lowest oxidation states of metals leading to the formation of complexes of Tc^I, Tc^{II} and Tc^{III}. Nevertheless, using the appropriate stoichiometric ratio, dioxotechnetium(V) phosphine complexes have been obtained, but solely with tertiary diphosphines.[2] On the other hand, many mono- and di-oxorhenium(V) phosphine complexes are known, since they can be prepared straightforwardly by ligand-exchange reaction from various oxorhenium(V) complexes upon addition of the suitable phosphine. In addition, primary aliphatic diamines, cyclic secondary amines, pyridines and imidazole form dioxo complexes of Tc^V and Re^V.[3–5] In a previous paper we reported the reactivity of bidentate phosphine–carboxylic ligands of the type PPh_2RCO_2H, where R = CH_2, C_2H_4 or *o*-C_6H_4, with pertechnetate obtaining only homoleptic technetium(III) complexes.[6]

We now report on the synthesis and reactivity at different pH of monooxometal(V) (M = Tc or Re) complexes with the ligand HL. To our knowledge, the technetium(V) complexes, directly

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[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

prepared from pertechnetate, are the first mixed-ligand complexes containing tertiary phosphines and amines. Two series of compounds have been fully characterized. The first contains two L$^-$ ligands symmetrically co-ordinated in the equatorial plane (named 'equatorial') and an alkoxo coligand *trans* to the oxo moiety. The second, peculiar to rhenium (named 'twisted'), have one equatorial L$^-$ ligand and another twisted by 90° with the amido group bonded *trans* to the oxo moiety and a halide as coligand. In all the products of both series the phosphorus atom of the two ligands is *cis*-co-ordinated. Synthetic differences and a comparison of the behaviours of Tc *vs.* Re are described. The infrared spectra of most of the complexes exhibit unusual very low values of the M=O stretches, those of the 'equatorial' ones being below 900 cm^{-1}. The crystal structures of 'equatorial' [TcOL$_2$(OMe)] **1**, [ReOL$_2$(OEt)] **5** and 'twisted' [ReOL$_2$Cl] **12** and **13** are reported, the last being present in two crystal systems.

Experimental

Apparatus.—**CAUTION**: Technetium-99 is a weak β emitter (E_{max} = 0.292 MeV, *ca.* 4.67 × 10^{-17} J) with $t_{\frac{1}{2}}$ = 2.12 × 10^5 years. All manipulations were carried out in glove-boxes, in a laboratory approved for low-level radioactivity.

Microanalyses were carried out on a model 1106 Carlo Erba elemental analyser. Moreover, only for 'twisted' rhenium samples, spot or selected area analyses, to determine the Re:P:X (X = Cl, Br or I) ratios, were performed by integral counting of the back-scattered X-ray fluorescence radiation from a Philips model XL 40 scanning electron microscope equipped with an EDAX model data station. Samples for scanning electron microscopy (SEM) analyses were prepared by suspending the microcrystalline powders in Et$_2$O. A few drops of the resulting suspension were deposited on a graphite support and, after evaporation of the solvent, the samples were metallized with graphite in an Edward S150B sputter coater.[7] All samples revealed homogeneous microcrystals. Infrared spectra were recorded in Nujol mulls or KBr pellets on a Mattson 3030 Fourier-transform spectrometer (4000–220 cm^{-1}), electronic absorbtion spectra on a Cary 17D spectrometer (700–220 nm). Proton and ^{31}P NMR spectra were obtained on a Bruker AC-200 spectrometer using different solvents and SiMe$_4$ as internal reference and PPh$_3$ as external reference respectively (in deuteriochloroform PPh$_3$ resonates at δ −7.42 with respect to 85% H$_3$PO$_4$ in D$_2$O). Positive-ion fast atom bombardment (FAB$^+$) mass spectra were recorded on a VG ZAB-2F instrument (8 keV Xe atoms bombarding 3-nitrobenzyl alcohol solutions of samples). Unless otherwise stated, conductivity measurements were carried out in MeCN at 293 K on a model E518 Metrohm Herison conductimeter.

Materials.—Technetium, as [NH$_4$][TcO$_4$] in 0.1 mol dm^{-3} ammonia solution, was supplied by the Radiochemical Centre, Amersham. Solid [NH$_4$][TcO$_4$] was obtained by taking to dryness small aliquots of this solution. The salt [NBu$_4$][TcO$_4$] was obtained by metathesis, as a crystalline precipitate, from aliquots of ammonia solutions of [NH$_4$][TcO$_4$] by addition of excess of [NBu$_4$]Cl. The salts [NBu$_4$][MOCl$_4$], [ReO$_2$(py)$_4$]Cl (py = pyridine) and [NBu$_4$][ReO(eg)$_2$] (H$_2$eg = ethylene glycol) were prepared as reported previously.[8] All common laboratory chemicals were of reagent grade and used without further purification. Solvent, for UV/VIS spectra were of UV/VIS grade. The ligand HL was prepared according to the method reported by Cooper *et al.*[9] All the syntheses were carried out under aerobic conditions.

Preparation of the Complexes.—[TcOL$_2$(OR)] (R = Me **1** *or* Et **2**). The salt [NBu$_4$][TcO$_4$] (42 mg, 0.1 mmol) was dissolved in ROH (R = Me or Et) (3 cm^3); to the solution was added HL (86 mg, 0.3 mmol) dissolved in ROH (2 cm^3). The solution was stirred at room temperature for 24 h during which it turned from the initial pale violet to the final brown-red. The solid precipitated was filtered off, washed three times with a total of 4.5 cm^3 of alcohol and finally dried under a nitrogen stream. Yields: **1**, 45 mg, 64%; **2**, 43 mg, 59% (Found: C, 62.8; H, 4.6; N, 3.8. C$_{37}$H$_{33}$N$_2$O$_2$P$_2$Tc **1** requires C, 63.60; H, 4.75; N, 4.0. Found: C, 63.5; H, 4.7; N, 3.8. C$_{38}$H$_{35}$N$_2$O$_2$P$_2$Tc **2** requires C, 64.05; H, 4.95; N, 3.95%). The products are soluble in MeCN, CH$_2$Cl$_2$, CHCl$_3$, Me$_2$CO and dimethylformamide (dmf), slightly soluble in MeOH and EtOH, insoluble in Et$_2$O and hydrocarbons. Molar conductivity: Λ_M = 18 (**1**), 15 ohm^{-1} cm^2 mol^{-1} (**2**). FAB mass spectrum for both complexes: *m/z* 668 [*M* − OR]$^+$. UV/VIS bands in CH$_2$Cl$_2$–ROH (10:90): **1**, 510 (5360), 415 (7600) and 350 (7600); **2**, 485 (8270) and 335 nm (ε = 6360 dm^3 mol^{-1} cm^{-1}).

[ReOL$_2$(OH)] **3**. Compound **12** or **13** (30 mg, 0.038 mmol) was dissolved in the minimum amount of CH$_2$Cl$_2$, then MeCN (3 cm^3) added along with NEt$_3$ (0.5 cm^3, 3.6 mmol). The mixture was taken to reflux for 10 min, then water (2 cm^3) was added; the colour turned from green to orange-brown. The mixture was reduced to 3 cm^3 by boiling, then left to cool. Overnight an orange powder precipitated, it was filtered off, washed with water (2 cm^3) and finally dried under vacuum (yield 24 mg, 82%) (Found: C, 56.3; H, 4.1; N, 3.5. C$_{36}$H$_{31}$N$_2$P$_2$O$_2$Re requires C, 56.00; H, 4.05; N, 3.65%). The product is soluble in alcohols (where it transforms into the corresponding OR derivatives), CH$_2$Cl$_2$, CHCl$_3$ (decomposes partially to the starting [ReOL$_2$Cl] complex), slightly soluble in MeCN and Me$_2$CO, insoluble in Et$_2$O and water. Molar conductivity Λ_M = 12 ohm^{-1} cm^2 mol^{-1}. UV/VIS spectrum in MeCN: 395 (10 150) and 320 nm (ε = 13 500 dm^3 mol^{-1} cm^{-1}); compounds **4**–**11** have similar spectra.

[ReOL$_2$(OMe)] **4**. The salt [NBu$_4$][ReOCl$_4$] (102 mg, 0.17 mmol) was dissolved in the minimum amount of MeOH, and H$_2$eg (0.5 cm^3) followed by NaO$_2$CMe (1.5 cm^3, 0.75 mol dm^{-3} in MeOH) were added dropwise. To the brown-violet mixture HL (145 mg, 0.34 mmol) was added; while the ligand was dissolving the solution turned brown. After 2 h of stirring, at room temperature, the orange-brown solid was filtered off, washed (three times) with MeOH (1 cm^3) and dried under vacuum. Yield 105 mg, 78% (Found: C, 56.7; H, 4.3; N, 3.5. C$_{37}$H$_{33}$N$_2$O$_2$P$_2$Re requires C, 56.55; H, 4.25; N, 3.55%). The solid is soluble in CH$_2$Cl$_2$, CHCl$_3$, MeCN, dmf and Me$_2$CO, slightly soluble in Et$_2$O and EtOH, and insoluble in MeOH and hydrocarbons. Molar conductivity, Λ_M = 8 ohm^{-1} cm^2 mol^{-1}.

[ReOL$_2$(OEt)] **5**. The salt [NBu$_4$][ReOCl$_4$] (112 mg, 0.19 mmol) was dissolved in EtOH (4 cm^3), and H$_2$eg (0.5 cm^3) and NEt$_3$ (0.3 cm^3, 2.0 mmol) were added. To the violet-brown solution HL (105 mg, 0.38 mmol) was added, and the colour turned green and then brown-orange. After 1 h of stirring, at room temperature, the orange-brown solid was filtered off, washed twice with EtOH (1 cm^3) and dried under vacuum (yield 122 mg, 81%) (Found: C, 57.3; H, 4.5; N, 3.4. C$_{38}$H$_{35}$N$_2$O$_2$P$_2$Re requires C, 57.05; H, 4.40; N, 3.50%). The crystals are soluble in CH$_2$Cl$_2$, CHCl$_3$, MeCN, dmf and Me$_2$CO, slightly soluble in Et$_2$O, insoluble in EtOH, MeOH and hydrocarbons. Molar conductivity, Λ_M = 10.5 ohm^{-1} cm^2 mol^{-1}. The crystal structure was determined for crystals grown from a CH$_2$Cl$_2$ solution layered with EtOH.

[ReOL$_2$(OR)] (R = Pr **6** *or* Bu **7**). Complex **4** (40 mg, 0.051 mmol) was dissolved in the minimum volume of CH$_2$Cl$_2$ in a test-tube, and layered alternatively with propanol or butanol (8 cm^3). After 3 d, upon mutual diffusion of solvents, brown crystals formed (average yield 35%) (Found: C, 57.1; H, 4.3; N, 3.4. C$_{39}$H$_{37}$N$_2$O$_2$P$_2$Re **6** requires C, 57.55; H, 4.60; N, 3.45. Found: C, 57.5; H, 4.5; N, 3.2. C$_{40}$H$_{39}$N$_2$O$_2$P$_2$Re **7** requires C, 58.05; H, 4.75; N, 3.40%). The compounds are soluble in CH$_2$Cl$_2$, CHCl$_3$, slightly soluble in MeCN, dmf and Me$_2$CO, insoluble in Et$_2$O and water. Molar conductivity, Λ_M = 8 (**6**) and 10 ohm^{-1} cm^2 mol^{-1} (**7**).

[ReOL$_2$(OR)] (R = C$_2$H$_4$OH **8** *or* C$_3$H$_6$OH **9**). The salt

$[NBu_4][ReOCl_4]$ (70 mg, 0.12 mmol) was dissolved in MeCN (5 cm^3) and NEt_3 (0.2 cm^3) was added along with the glycol (0.5 cm^3, 10-fold excess) and HL (66 mg, 0.24 mmol). After stirring for 30 min the deep orange solids precipitated were filtered off, washed with a total of 2 cm^3 of MeCN followed by Et_2O, then dried under vacuum. Average yield 83% (Found: C, 56.0; H, 4.3; N, 3.4. $C_{38}H_{35}N_2O_3P_2Re$ **8** requires C, 55.95; H, 4.30; N, 3.45. Found: C, 56.8; H, 4.5; N, 3.4. $C_{39}H_{37}N_2O_3P_2Re$ **9** requires C, 56.45; H, 4.50; N, 3.35%). The compounds have the same solubility properties as those of **6**. Molar conductivity, $\Lambda_M = 13$ (**8**) and 11 ohm^{-1} cm^2 mol^{-1} (**9**).

$[ReOL_2(OPh)]$ **10**. Complex **4** (40 mg, 0.051 mmol) was dissolved in MeCN (5 cm^3) and PhOH (48 mg, 0.51 mmol) was added. Upon concentration, by slow evaporation in air, dark red needles were obtained, washed with MeCN (2 cm^3) and dried under vacuum (yield 10 mg, 23%) (Found: C, 59.7; H, 4.2; N, 3.6. $C_{42}H_{35}N_2O_2P_2Re$ requires C, 59.50; H, 4.15; N, 3.30%). The complex has the same solubility properties as those of **6**. Molar conductivity, $\Lambda_M = 15$ ohm^{-1} cm^2 mol^{-1}.

$[ReOL_2(O_2CMe)]$ **11**. Complex **13** (48 mg, 0.06 mmol) was dissolved in the minimum volume of CH_2Cl_2, MeCN (3 cm^3) was added along with NEt_3 (1.0 cm^3, 7.2 mmol). The mixture was refluxed for 10 min, then glacial acetic acid (0.41 cm^3, 7.2 mmol) was added. After refluxing for 30 min, during which the colour turned orange-brown, the volume of the mixture was reduced to 3 cm^3 by boiling. Upon standing overnight, orange-brown crystals formed. They were filtered off, washed with MeCN (2 cm^3) followed by water (5 cm^3) (yield 35 mg, 73%) and dried under vacuum (Found: C, 55.8; H, 3.9; N, 3.3. $C_{38}H_{33}N_2O_3P_2Re$ requires C, 56.10; H, 4.10; N, 3.45%). The complex, except for Me_2CO in which it is soluble, has the same solubility properties as those of compound **6**. Molar conductivity in MeCN–Me_2CO (70:30 v/v), $\Lambda_M = 9$ ohm^{-1} cm^2 mol^{-1}.

α-$[ReOL_2Cl]$ **12**. The salt $[NBu_4][ReOCl_4]$ (120 mg, 0.2 mmol) was dissolved in MeOH (3 cm^3), and HL (111 mg, 0.4 mmol) solubilized in MeOH (2 cm^3) was added; the initial green solution turned green-brown. After stirring for 1 h the solution became clear and the dark solid present was filtered off, washed with a total of 4.5 cm^3 (three aliquots) of MeOH and finally dried under vacuum (yield 150 mg, 95%) (Found: C, 54.6; H, 3.9; N, 3.5. $C_{36}H_{30}CN_2OP_2Re$ requires C, 54.70; H, 3.80; N, 3.55%). SEM microanalyses 1:2:1 (Re:P:Cl) ratio. The product is soluble in CH_2Cl_2 and $CHCl_3$, slightly soluble in benzene, toluene, Me_2CO and MeCN, insoluble in Et_2O, MeOH, EtOH and hydrocarbons. Molar conductivity in MeCN–CH_2Cl_2 (90:10 v/v), $\Lambda_M = 15.3$ ohm^{-1} cm^2 mol^{-1}. FAB mass spectrum: *m/z* 755 $[M - Cl]^+$; identical parent ion peak shown by all 'twisted' complexes. UV/VIS bands in CH_2Cl_2: 620 (sh), 450 (7300), 405 (6950) and 320 nm ($\varepsilon = 10\,300$ dm^3 mol^{-1} cm^{-1}). Good crystals for crystal structure determination were grown from a CH_2Cl_2 solution layered with MeOH.

β-$[ReOL_2Cl]$ **13**. The complex was prepared as for product **12**, but in EtOH, MeCN or Me_2CO. Yield 94% (Found: C, 54.2; H, 3.8; N, 3.5. $C_{36}H_{30}ClN_2OP_2Re$ requires C, 54.70; H, 3.80; N, 3.55%). SEM microanalyses 1:2:1 (Re:P:Cl) ratio. The complex possesses UV/VIS properties and molar conductivity identical to those of **12**. Crystals for structure determination were obtained as for **12**, but from CH_2Cl_2–EtOH.

$[ReOL_2Br]$ **14**. Complex **4** (32 mg, 0.04 mmol) was dispersed in EtOH or MeOH (3 cm^3) and 48% HBr (50 μl, 0.45 mmol) was added under vigorous stirring. The mixture turned from orange-brown to green and, within 2 min, a black solid formed leaving the solution completely clear. It was filtered off, washed with EtOH (3 cm^3) followed by Et_2O (2 cm^3) and dried under vacuum (yield 33 mg, 97%) (Found: C, 50.8; H, 3.7; N, 3.2. $C_{36}H_{30}BrN_2OP_2Re$ requires C, 51.8; H, 3.60; N, 3.35%). SEM microanalyses 1:2:1 (Re:P:Br) ratio. The product is soluble in CH_2Cl_2, slightly soluble in $CHCl_3$, MeCN and Me_2CO, insoluble in MeOH, EtOH, Et_2O and hydrocarbons. Molecular conductivity in MeCN–CH_2Cl_2 (90:10 v/v), $\Lambda_M = 9$ ohm^{-1} cm^2 mol^{-1}. UV/VIS bands in CH_2Cl_2: 610 (sh), 465 ($\varepsilon = 8590$ dm^3 mol^{-1} cm^{-1}), 393 (8220) and 320 (11 530) nm.

$[ReOL_2I]$ **15**. The complex, a dark solid, was prepared with the same procedure as for the bromide except that 57% HI was used (yield 34 mg, 97%) (Found: C, 48.5; H, 3.5; N, 3.1. $C_{36}H_{30}IN_2OP_2Re$ requires C, 49.05; H, 3.45; N, 3.15%). SEM microanalyses 1:2:1 (Re:P:I) ratio. The compound is soluble in CH_2Cl_2, slightly soluble in $CHCl_3$, MeCN and Me_2CO, insoluble in MeOH, EtOH, Et_2O and hydrocarbons. Molar conductivity in MeCN–CH_2Cl_2 (90:10 v/v), $\Lambda_M = 8$ ohm^{-1} cm^2 mol^{-1}. UV/VIS bands in CH_2Cl_2: 620 (sh), 480 (6900), 390 ($\varepsilon = 8280$ dm^3 mol^{-1} cm^{-1}) and 310 nm (sh).

Crystallography.—Details of the crystal data, intensity measurement and data processing for the four structures are summarized in Table 1. Cell parameters were determined from 50 high-angle data ($2\theta > 23°$). For the calculation of the structure factors, corrections for Lorentz polarization effects and absorption (using an empirical method based on ψ scans of six reflections at $\chi \approx 90°$) were made. The structures were solved by standard heavy-atom methods to locate the heavy and P atoms with subsequent Fourier difference maps yielding the positions of the remaining non-hydrogen atoms. The hydrogens were included in calculated positions but were not refined. To ensure a good observation/variable ratio and to achieve convergence, for complex **1** only Tc and P atoms were refined anisotropically, while for **12** and **13** the carbon atoms far from the inner core were treated isotropically. Difference maps, calculated after the refinement, were essentially featureless, the largest peaks being 0.6 (0.8 Å from Tc) for **1**, 0.8 (0.9 Å from Re) for **5**, 1.3 (0.9 Å from Re) for **12** and 1.4 e $Å^{-3}$ (0.9 Å from Re) for **13**. Fractional atomic coordinates for the four complexes are given in Table 2, selected bond distances and angles in Table 3. The SHELXTL-PLUS package[10] of computer programs was employed for the solution and refinement of the four structures.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Synthesis, Characterization and Reactivity.—Technetium complexes. The ligand HL reacts with $[NBu_4][TcO_4]$ at room temperature in 1:3 (Tc:HL) ratio producing 'equatorial' $[Tc^VOL_2(OR)]$ type complexes.* All the complexes are neutral and were characterized by the usual chemicophysical techniques, $[TcOL_2(OMe)]$ by crystal structure determination, and by comparison with the analogous oxorhenium(V) complexes. Varying the reaction conditions (*i.e.* by changing the solvent or the pertechnetate counter anion) led to different products. In protic solvents, like MeOH or EtOH, in which $[NBu_4][TcO_4]$ is highly soluble the addition of a three-fold molar excess of ligand results in the stoichiometry (1). When $[NH_4][TcO_4]$ is used as starting material, owing to its low solubility in alcohols, the stoichiometric ratio increases in favour of the HL ligand and the reaction occurs following the alternative route (2). If the reaction is carried out either with $[NR_4][TcO_4]$ (R = H or Bu) in aprotic solvents such as MeCN or Me_2CO the complex $[Tc^{III}L_3]$ is always the main product. Furthermore, in superior

$$[NBu_4][Tc^{VII}O_4] + 3HL + ROH \longrightarrow [Tc^VOL_2(OR)] + O(HL) + NBu_4OH + H_2O \quad (1)$$

$$[NH_4][Tc^{VII}O_4] + 5HL \longrightarrow [Tc^{III}L_3] + 2O(HL) + NH_4OH + H_2O \quad (2)$$

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* The product $[TcOL_2(OMe)]$ was first recovered as a side product in the preparation of $[Tc^{III}(HL)L_2][O_2CCF_3]$, upon increasing the pH above 11 by addition of 5% NaOH to the mother liquor (see ref. 1).

Table 1 Structure determination summary *

	1	5	12	13
Crystal data				
Empirical formula	$C_{37}H_{33}N_2O_2P_2Tc$	$C_{38}H_{35}N_2O_2P_2Re$	$C_{36}H_{30}ClN_2OP_2Re$	$C_{36}H_{30}ClN_2OP_2Re$
M	697.6	799.8	790.2	790.2
Colour, habit	Dark purple hexagonal plates	Dark orange parallelepipeds	Violet parallelepipeds	Brown hexagonal prisms
Crystal size/mm	0.24 × 0.20 × 0.04	0.15 × 0.15 × 0.25	0.12 × 0.18 × 0.24	0.20 × 0.30 × 0.10
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
a/Å	12.156(3)	12.056(3)	9.594(1)	10.196(5)
b/Å	26.005(6)	26.303(6)	18.565(4)	14.047(6)
c/Å	10.953(2)	11.005(3)	17.656(2)	21.987(8)
β/°	102.49(2)	102.32(2)	91.00(1)	
U/Å^3	3377.1(1.6)	3409.4(1.4)	3145.4(1.5)	3149.1(2.0)
Z	4	4	4	4
D_c/Mg m^{-3}	1.37	1.56	1.67	1.67
μ/mm^{-1}	0.54	3.74	4.13	4.13
F(000)	1432	1592	1560	1560
Data collection				
2θ Range/°	3.0–40.0	4.0–55.0	4.0–45.0	4.0–50.0
Index ranges	$0 < h < 11, -24 < k < 0, -10 < l < 10$	$0 < h < 15, -34 < k < 0, -14 < l < 13$	$-10 < h < 10, 0 < k < 20, 0 < l < 19$	$0 < h < 12, 0 < k < 16, 0 < l < 26$
Reflections collected	3480	8415	4466	3175
Independent reflections	3178	7882	4143	3152
Observed reflections $[F_o > 4\sigma(F_o)]$	1766	4752	2979	2501
Solution and refinement				
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.001F^2$	$\sigma^2(F) + 0.0012F^2$	$\sigma^2(F) + 0.0006F^2$	$\sigma^2(F) + 0.0022F^2$
Number of parameters refined	192	407	286	286
Final R,R' (obs. data)	0.0575, 0.0611	0.0509, 0.0614	0.0426, 0.0477	0.0534, 0.0671
Goodness of fit	1.19	0.88	1.24	1.20

* Details in common: Siemens R3 m/V diffractometer; Mo-Kα radiation (λ = 0.710 73 Å); T 294 K; highly oriented graphite-crystal monochromator; ω–2θ scans; ω scan speed 4.50–14.65° min^{-1}; scan range 0.60° + Kα separation; stationary crystal and counter at beginning and end of scan, each for 25% of total scan time; two standard reflections every 100; refinement by full-matrix least squares minimizing $\Sigma w(|F_o| - |F_c|)^2$; riding model used for H atoms with common variable U.

(*i.e.* propanol or butanol) or branched alcohols (*i.e.* Pr^{i}OH or Bu^{t}OH), even after 36 h of reaction, [Tc^{III}L$_3$] (yield 10%) together with unreacted [NBu$_4$][TcO$_4$] are always recovered from the reaction mixture. Reaction (1), performed in MeCN and water (few drops), leads to uncharacterized red-violet solutions; any attempt to precipitate a solid ended with the recovery of unreacted pertechnetate. In reaction (1) pertechnetate is reduced to oxotechnetium(V) by 1 mol of the HL ligand which is in turn oxidized to the phosphine oxide[11] (detectable by ^{31}P NMR spectroscopy of aliquots of the mother liquor).

Although the autogenous pH of the reaction medium is basic, because of the presence of the ancillary aniline group, the bidentate HL ligand co-ordinates as a mononegative anion and an alkoxide saturates the sixth position *trans* to the oxo moiety, yielding neutral six-co-ordinated oxotechnetium(V) complexes. Even though the reaction is performed in the presence of an excess of chloride salt (*i.e.* NBu$_4$Cl) it never produces any chloro derivative. On the other hand, when it is carried out in ROH using [NBu$_4$][Tc^{V}OCl$_4$] in 1:2 (Tc:HL) ratio the phosphine reduces the starting material and a yellow crystalline product is recovered. The Tc=O stretching is absent in the IR spectrum and the FAB$^+$ mass spectrum, m/z = 722 ([M]$^+$), 687 ([M − Cl]$^+$) and 652 ([M − 2Cl]$^+$) is consistent with 1 Tc, 2 ligands, 2 Cl. An identical product is obtained when dilute HCl is added to either the complexes [Tc^{V}OL$_2$(OR)] or [Tc^{III}L$_3$]. When a non-co-ordinating acid (*i.e.* CF$_3$CO$_2$H or CF$_3$SO$_3$H) is added to a [Tc^{V}OL$_2$(OR)] solution again the blue cationic [Tc^{III}(HL)L$_2$]$^+$ is recovered.[1]

The complex [TcOL$_2$(OEt)] is quite stable in the solid state, while [TcOL$_2$(OMe)] shows signs of decomposition: over a couple of weeks a further strong absorption at 900 cm^{-1} due to pertechnetate occurs in the IR spectrum. However, both complexes slowly decompose in solution; a few crystals of [TcOL$_2$(OMe)] were collected from an acetonitrile solution and used for the X-ray analysis. The co-ordination of two L$^-$ ligands is revealed, apart from the elemental analysis, by the disappearance, in the IR spectrum, of the band at 1607 cm^{-1} corresponding to the bending of NH$_2$ of the free ligand, while the presence of only one N–H stretching indicates the co-ordination, in symmetrical fashion, of two monoanionic chelating ligands. The Tc=O stretches (Table 4) show a difference of 21 cm^{-1}, being weaker than that of the ethanolate complex. The FAB$^+$ mass spectra for both compounds show the presence of a peak with m/z 668 which indicates the loss of the alcoholate coligand.

Rhenium complexes. A number of rhenium complexes have been prepared, depending on the oxorhenium(V) starting material and the pH of the reaction medium employed. All the syntheses can be performed by ligand-exchange reactions, at room temperature, since the reaction pathway is not affected by heating or refluxing. The ligand is used in double stoichiometric amount with respect to rhenium. The direct ligand reaction with [NBu$_4$][ReO$_4$] in 1:5 (Re:HL) ratio was attempted, but even upon refluxing in EtOH overnight no reaction occurred; only upon addition of CF$_3$SO$_3$H an oily product, soluble in all common solvents except water, was recovered, but in its IR spectrum the Re=O stretching was absent.[12] The 'equatorial' complexes of the type [ReOL$_2$(OR)] are themselves good starting materials; for instance, the ethoxo, n-propoxo, n-butoxo, phenolate and the acetate derivatives can be prepared merely by dissolving [ReOL$_2$(OMe)] in CH$_2$Cl$_2$ or MeCN followed by addition of the appropriate nucleophile. Further-

Table 2 Atomic coordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) Complex **1**							
Tc	982(1)	−721(1)	921(1)	C(15)	4828(13)	−1612(6)	5194(15)
P(1)	2595(3)	−682(2)	2788(3)	C(16)	4842(13)	−2016(6)	4510(14)
P(2)	−6(3)	−1570(1)	794(3)	C(17)	4265(13)	−2063(6)	3298(15)
O(1)	114(6)	−508(3)	1839(7)	C(18)	3578(12)	−1640(6)	2789(14)
O(2)	2110(6)	−1170(3)	353(7)	C(19)	2279(10)	−367(5)	4165(12)
C(37)	2598(12)	−1062(5)	−713(13)	C(20)	2845(12)	78(5)	4700(13)
N(1)	1775(8)	−107(4)	499(9)	C(21)	2549(12)	306(6)	5724(14)
N(2)	37(7)	−681(4)	−789(8)	C(22)	1735(12)	85(6)	6219(15)
C(1)	3452(10)	−232(5)	2123(11)	C(23)	1148(13)	−329(6)	5736(15)
C(2)	2882(11)	17(5)	1058(12)	C(24)	1441(11)	−569(5)	4685(13)
C(3)	3432(12)	409(5)	508(13)	C(25)	651(10)	−2195(5)	922(11)
C(4)	4542(14)	516(6)	1047(15)	C(26)	1425(12)	−2299(6)	179(13)
C(5)	5117(13)	266(6)	2119(14)	C(27)	1953(13)	−2772(6)	260(14)
C(6)	4573(12)	−125(6)	2656(14)	C(28)	1793(12)	−3144(6)	1070(13)
C(7)	−789(10)	−1521(4)	−806(11)	C(29)	980(13)	−3050(6)	1759(14)
C(8)	−669(10)	−1051(5)	−1368(11)	C(30)	446(12)	−2578(6)	1718(13)
C(9)	−1349(11)	−965(5)	−2601(12)	C(31)	−1054(10)	−1609(4)	1741(11)
C(10)	−2055(11)	−1358(5)	−3139(13)	C(32)	−684(11)	−1629(5)	3045(12)
C(11)	−2143(12)	−1817(6)	−2609(14)	C(33)	−1462(11)	−1671(5)	3821(13)
C(12)	−1495(11)	−1900(5)	−1415(13)	C(34)	−2556(13)	−1667(5)	3316(14)
C(13)	3528(11)	−1207(5)	3469(13)	C(35)	−2957(13)	−1646(5)	2055(13)
C(14)	4133(12)	−1196(6)	4693(14)	C(36)	−2202(11)	−1619(5)	1255(12)
(*b*) Complex **5**							
Re	901(1)	749(1)	916(1)	C(17)	2469(13)	−258(6)	5680(10)
P(1)	2511(2)	713(1)	2765(2)	C(18)	2766(10)	−44(4)	4641(10)
P(2)	−154(2)	1569(1)	798(2)	C(19)	3390(7)	1245(4)	3458(9)
O(1)	36(5)	511(2)	1802(6)	C(20)	3425(9)	1690(5)	2779(11)
O(2)	2036(5)	1195(3)	342(6)	C(21)	4089(10)	2099(6)	3301(13)
N(1)	1760(6)	150(3)	505(7)	C(22)	4704(10)	2070(6)	4506(14)
N(2)	−61(7)	701(3)	−805(7)	C(23)	4674(11)	1636(5)	5175(13)
C(1)	3403(8)	280(4)	2123(9)	C(24)	4036(9)	1221(5)	2687(10)
C(2)	4546(10)	177(6)	2639(12)	C(25)	475(8)	2207(4)	909(8)
C(3)	5124(12)	−195(6)	2094(13)	C(26)	1235(9)	2322(5)	172(11)
C(4)	4556(13)	−449(5)	1056(14)	C(27)	1746(9)	2793(5)	243(11)
C(5)	3444(10)	−346(5)	521(12)	C(28)	1542(10)	3151(5)	1074(10)
C(6)	2860(9)	30(5)	1047(10)	C(29)	769(11)	3038(5)	1798(12)
C(7)	−954(8)	1530(4)	−798(9)	C(30)	267(10)	2565(4)	1714(10)
C(8)	−1682(8)	1905(5)	−1410(10)	C(31)	−1213(8)	1595(4)	1767(8)
C(9)	−2320(10)	1810(6)	−2577(11)	C(32)	−2374(8)	1579(5)	1269(10)
C(10)	−2239(10)	1344(5)	−3167(10)	C(33)	−3128(11)	1602(6)	2065(14)
C(11)	−1462(9)	985(5)	−2579(9)	C(34)	−2744(12)	1646(5)	3332(12)
C(12)	−802(8)	1060(4)	−1381(9)	C(35)	−1590(11)	1647(4)	3821(10)
C(13)	2218(9)	390(4)	4122(9)	C(36)	−827(9)	1626(4)	3039(9)
C(14)	1375(10)	590(5)	4661(10)	C(37)	2505(9)	1095(4)	−711(10)
C(15)	1108(13)	366(7)	5697(12)	C(38)	3404(10)	1495(5)	−803(13)
C(16)	1651(13)	−56(7)	6231(13)				
(*c*) Complex **12**							
Re	695(1)	840(1)	3700(1)	C(16)	1242(15)	982(8)	235(9)
Cl	1576(3)	1074(1)	4979(2)	C(17)	−104(17)	857(8)	328(9)
P(1)	−282(3)	274(2)	2569(2)	C(18)	−639(15)	631(7)	1023(8)
P(2)	−632(3)	1984(2)	3635(2)	C(19)	−2167(10)	177(6)	2549(6)
O	2042(7)	1289(4)	3219(4)	C(20)	−2763(12)	−418(6)	2871(6)
N(1)	1282(9)	−171(5)	3889(5)	C(21)	−4252(13)	−452(8)	2970(7)
N(2)	−1182(9)	580(5)	4136(5)	C(22)	−5028(15)	119(7)	2755(8)
C(1)	406(11)	−628(6)	2692(6)	C(23)	−4454(13)	715(7)	2428(7)
C(2)	317(11)	−1184(7)	2166(7)	C(24)	−3017(12)	745(6)	2329(6)
C(3)	868(12)	−1862(7)	2327(8)	C(25)	−9(11)	2787(6)	4119(6)
C(4)	1497(11)	−1965(6)	3036(7)	C(26)	304(16)	3407(9)	3753(10)
C(5)	1628(12)	−1424(6)	3560(7)	C(27)	699(20)	4047(12)	4146(13)
C(6)	1097(10)	−732(6)	3399(6)	C(28)	929(16)	4012(8)	4898(9)
C(7)	−2250(10)	1740(6)	4054(5)	C(29)	650(14)	3406(8)	5269(8)
C(8)	−3396(12)	2191(7)	4190(6)	C(30)	177(12)	2789(7)	4888(7)
C(9)	−4627(13)	1914(8)	4458(7)	C(31)	−1005(10)	2304(5)	2675(5)
C(10)	−4706(12)	1193(8)	4625(7)	C(32)	49(11)	2299(6)	2155(6)
C(11)	−3585(11)	733(7)	4531(6)	C(33)	−188(12)	2534(7)	1425(7)
C(12)	−2342(9)	1006(6)	4242(5)	C(34)	−1499(11)	2737(6)	1189(7)
C(13)	274(12)	548(6)	1630(6)	C(35)	−2565(11)	2749(6)	1693(6)
C(14)	1668(14)	687(7)	1533(8)	C(36)	−2324(10)	2526(6)	2428(6)
C(15)	2137(18)	899(9)	825(9)				

Table 2 (*continued*)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*d*) Complex **13**							
Re	1280	−415	1387	C(16)	482(26)	1011(20)	−1247(13)
O	2426(13)	93(10)	940(7)	C(17)	−778(24)	1078(18)	−1012(12)
Cl	2721(6)	−880(4)	2211(3)	C(18)	−1034(24)	644(16)	−460(11)
P(1)	−387(4)	−373(3)	595(2)	C(19)	−2034(17)	6(12)	805(7)
P(2)	865(5)	1150(3)	1868(2)	C(20)	−3006(19)	−661(14)	914(10)
N(1)	1168(19)	−1807(10)	1190(7)	C(21)	−4219(32)	−370(26)	1127(15)
N(2)	−353(13)	−634(9)	1901(7)	C(22)	−4420(22)	589(15)	1271(10)
C(1)	−494(18)	−1634(12)	417(7)	C(23)	−3450(19)	1225(16)	1145(9)
C(2)	−1265(22)	−2012(12)	−48(8)	C(24)	−2293(20)	965(14)	946(9)
C(3)	−1246(24)	−3006(12)	−157(9)	C(25)	2047(17)	1586(12)	2427(9)
C(4)	−441(23)	−3554(13)	198(10)	C(26)	3182(18)	2006(13)	2239(9)
C(5)	373(20)	−3190(13)	664(9)	C(27)	4074(19)	2275(15)	2640(10)
C(6)	402(16)	−2196(11)	767(7)	C(28)	3829(25)	2156(15)	3281(10)
C(7)	−661(16)	961(13)	2251(8)	C(29)	2785(26)	1748(19)	3455(13)
C(8)	−1412(22)	1634(13)	2537(8)	C(30)	1844(22)	1446(16)	3055(10)
C(9)	−2609(18)	1402(16)	2813(10)	C(31)	739(16)	2187(10)	1364(9)
C(10)	−3051(22)	468(17)	2776(9)	C(32)	973(19)	2099(14)	758(9)
C(11)	−2295(20)	−208(14)	2488(9)	C(33)	831(23)	2827(19)	350(13)
C(12)	−1130(21)	18(11)	2213(7)	C(34)	434(27)	3694(21)	579(13)
C(13)	−73(21)	198(13)	−136(9)	C(35)	278(26)	3845(21)	1186(12)
C(14)	1224(27)	117(16)	−399(10)	C(36)	395(22)	3061(16)	1563(10)
C(15)	1468(25)	556(17)	−959(11)				

more, 'equatorial' [ReOL$_2$(OR)] produce, by addition of the appropriate HX, the complexes of the 'twisted' series [ReOL$_2$X] (see below). All 'equatorial' rhenium compounds present identical UV/VIS spectra in MeCN or CH$_2$Cl$_2$, unchanged even when recorded in the presence of the corresponding nucleophilic reagent. The FAB$^+$ mass spectra always show the ion [ReOL$_2$]$^+$ at m/z = 755 for both 'equatorial' and 'twisted' complexes.

(*a*) *Syntheses in basic media: 'equatorial'* [ReOL$_2$(OR)]. (*i*) *In protic solvents*. The compound [ReOL$_2$(OMe)] is obtained from [ReO(eg)$_2$]$^-$ prepared *in situ* starting from [NBu$_4$][ReOCl$_4$] in MeOH and NaO$_2$CMe; the ligand is used in a 1:2 (Re:HL) ratio. The analogous ethoxo derivative [ReOL$_2$(OEt)] is synthesised by using NEt$_3$ and EtOH as reaction solvent, while compounds **6** and **7** were obtained by simple recrystallization of [ReOL$_2$(OMe)] from CH$_2$Cl$_2$–ROH. The co-ordination of two monoanionic ligands is revealed as for the technetium analogues. The ethoxo derivative was fully characterized by X-ray crystal analysis. The presence in all the IR spectra of a strong absorption in the region typical for the Re=O stretching confirms that the oxo moiety is always retained in a neutral rhenium(v) octahedral complex. The Re=O stretches occur at 887–902 cm^{-1}. As usual, the rhenium compounds exhibit higher values in comparison to the technetium ones. The IR spectra present a distinguishable sharp band corresponding to the N–H vibration near 3300 cm^{-1}. The C–H aliphatic stretches of the alcoholates give rise to a number of bands in the region 2800–3000 cm^{-1}.

(*ii*) *In aprotic solvents*. When [NBu$_4$][ReOCl$_4$] is treated with the HL ligand in the presence of glycols in basic MeCN (by NEt$_3$) the glycolate co-ordinates, as well as alcoholate, *trans* to the Re=O moiety. However, when the *trans*-glycolate complexes are recrystallized in the presence of alcohols they again rearrange into the alkoxo complexes (see above). In their IR spectra the Re=O stretches occur at 882 and 913 cm^{-1} respectively for the H$_2$eg and the propane-1,2 diol derivative (Table 4). The hydroxo derivative [ReOL$_2$(OH)] is always present as an impurity when protic solvents are employed, but it can be prepared pure in high yield from a 'twisted' complex dissolved in a CH$_2$Cl$_2$–MeCN mixture and further addition of water. Its IR spectrum exhibits a quite intense sharp band attributable to ν(O–H) at 3599 cm^{-1} and a double ν(Re=O) band at 930 and 920 cm^{-1} (more intense). The complex [ReOL$_2$(O$_2$CMe)], prepared as described for the hydroxo derivative, shows in its IR spectrum the highest ν(Re=O) value of the series at 946 cm^{-1} and the presence of the acetate ligand is confirmed by the stretching of the co-ordinated carboxylate at 1622 cm^{-1}.

(*b*) *Syntheses in acid media: 'twisted'* [ReOL$_2$X]. The reaction of [NBu$_4$][ReOCl$_4$] with the ligand HL in 1:2 (Re:HL) ratio produces two complexes depending on the solvent used. The compound obtained in MeOH shows in the IR spectrum (Table 4) the ν(Re=O) stretching at 899 cm^{-1} and ν(Re–Cl) at 271 cm^{-1}. Two sharp N–H stretches, at 3333 and 3255 cm^{-1}, suggest non-equivalent co-ordination of the two L$^-$ ligands. However, when the reaction is carried out in EtOH, MeCN or Me$_2$CO, despite the resulting product showing the same elemental analyses and UV/VIS bands as that in MeOH, it shows slight, but significant differences in the IR spectrum: ν(Re=O) at 907 cm^{-1}, ν(Re–Cl) at 281 cm^{-1}. Moreover, a broad band for the N–H stretching, constituted by two poorly resolved peaks at 3335 and 3341 cm^{-1}, is present.

Compound **13** can be also prepared by starting from the 'equatorial' [ReOL$_2$(OR)] complexes upon treatment with dilute HCl in any of the above-mentioned solvents. Interestingly, **12** or **13** when dissolved in basic CH$_2$Cl$_2$ (by NEt$_3$) regenerates, upon addition of the appropriate ROH ligand, all the derivatives of the 'equatorial' series. As expected, the bromide and iodide derivatives are synthesised by replacing HCl with HBr or HI. There are insignificant differences in the Re=O stretches of the β-halide complexes from 907 (Cl) to 905 (I) cm^{-1}, while ν(Re–X) for Br and I fall at values out of the available instrument range. The conversion of **12** into **13** is possible by treatment with HCl in CH$_2$Cl$_2$–EtOH solution or by recrystallization from CH$_2$Cl$_2$–EtOH (10:90 v/v), but the inverse recrystallization in CH$_2$Cl$_2$–MeOH leads to no variations.

Proton and ^{31}P NMR Spectra.—The NMR data for all complexes are reported in Table 4. The technetium and rhenium 'equatorial' complexes exhibit similar proton spectra. In detail, aromatic protons of the co-ordinated ligands fall, as unresolved multiplets, in the δ 6.60–7.90 region, slightly deshielded with respect to those of the free HL ligand. A typical singlet at around δ 9.00 ± 0.40 is characteristic of the two equivalent amido protons. The remaining signals belong to the protons of the

Table 3 Selected bond lengths (Å) and angles (°)

(*a*) Complex **1**

Tc–P(1)	2.511(3)	Tc–P(2)	2.503(4)	P(2)–C(25)	1.804(13)	P(2)–C(31)	1.811(14)
Tc–O(1)	1.700(8)	Tc–O(2)	1.999(8)	O(2)–C(37)	1.447(17)	N(1)–C(2)	1.390(15)
Tc–N(1)	1.972(10)	Tc–N(2)	1.976(8)	N(2)–C(8)	1.352(15)	C(1)–C(2)	1.383(17)
P(1)–C(1)	1.820(14)	P(1)–C(13)	1.829(13)	C(7)–C(8)	1.391(17)		
P(1)–C(19)	1.829(14)	P(2)–C(7)	1.809(11)				
P(1)–Tc–P(2)	111.2(1)	P(1)–Tc–O(1)	88.9(2)	Tc–P(2)–C(31)	113.9(4)	C(7)–P(2)–C(31)	105.7(5)
P(2)–Tc–O(1)	88.1(3)	P(1)–Tc–O(2)	79.0(2)	C(25)–P(2)–C(31)	105.1(6)	Tc–O(2)–C(37)	124.5(7)
P(2)–Tc–O(2)	79.7(2)	O(1)–Tc–O(2)	158.3(3)	Tc–N(1)–C(2)	124.0(8)	Tc–N(2)–C(8)	126.0(8)
P(1)–Tc–N(1)	79.8(3)	P(2)–Tc–N(1)	162.7(3)	P(1)–C(1)–C(2)	114.4(9)	P(1)–C(1)–C(6)	123.7(10)
O(1)–Tc–N(1)	105.8(4)	O(2)–Tc–N(1)	89.8(4)	N(1)–C(2)–C(1)	121.6(12)	N(1)–C(2)–C(3)	118.5(11)
P(1)–Tc–N(2)	164.0(3)	P(2)–Tc–N(2)	79.6(3)	P(2)–C(7)–C(8)	114.0(8)	P(2)–C(7)–C(12)	124.1(9)
O(1)–Tc–N(2)	103.6(4)	O(2)–Tc–N(2)	91.9(4)	N(2)–C(8)–C(7)	122.3(10)	N(2)–C(8)–C(9)	120.4(11)
N(1)–Tc–N(2)	87.1(4)	Tc–P(1)–C(1)	96.6(4)	P(1)–C(13)–C(14)	122.1(11)	P(1)–C(13)–C(18)	119.5(10)
Tc–P(1)–C(13)	127.4(4)	C(1)–P(1)–C(13)	106.5(6)	P(1)–C(19)–C(20)	122.7(11)	P(1)–C(19)–C(24)	118.5(10)
Tc–P(1)–C(19)	115.1(4)	C(1)–P(1)–C(19)	106.4(6)	P(2)–C(25)–C(26)	118.1(10)	P(2)–C(25)–C(30)	124.1(11)
C(13)–P(1)–C(19)	102.8(6)	Tc–P(2)–C(7)	97.9(4)	P(2)–C(31)–C(32)	118.4(9)	P(2)–C(31)–C(36)	123.8(9)
Tc–P(2)–C(25)	126.3(4)	C(7)–P(2)–C(25)	105.6(5)				

(*b*) Complex **5**

Re–P(1)	2.495(2)	P(1)–C(1)	1.81(1)	Re–O(1)	1.692(7)	P(2)–C(25)	1.84(1)
Re–P(2)	2.493(3)	P(1)–C(13)	1.82(1)	Re–O(2)	2.004(7)	P(2)–C(31)	1.83(1)
Re–N(1)	1.990(8)	P(1)–C(19)	1.82(1)	N(1)–C(6)	1.37(1)	O(2)–C(37)	1.42(1)
Re–N(2)	2.003(7)	P(2)–C(7)	1.82(1)	N(2)–C(12)	1.36(1)	C(37)–C(38)	1.53(2)
P(1)–Re–P(2)	112.0(1)	Re–P(1)–C(1)	97.4(3)	P(2)–Re–O(2)	81.6(2)	Re–N(2)–C(12)	126.0(7)
P(1)–Re–N(1)	78.7(2)	P(1)–C(1)–C(6)	114.8(7)	N(1)–Re–N(2)	87.7(3)	N(2)–C(12)–C(7)	121.9(8)
P(1)–Re–N(2)	164.0(3)	Re–N(1)–C(6)	125.8(7)	N(1)–Re–O(1)	104.6(3)	Re–P(2)–C(25)	126.1(3)
P(1)–Re–O(1)	89.1(2)	N(1)–C(6)–C(1)	119.9(1.0)	N(1)–Re–O(2)	88.2(3)	Re–P(2)–C(31)	114.5(3)
P(1)–Re–O(2)	79.4(2)	Re–P(1)–C(13)	115.7(3)	N(2)–Re–O(1)	102.6(3)	Re–O(2)–C(37)	124.6(6)
P(2)–Re–N(1)	163.3(2)	Re–P(1)–C(19)	126.4(3)	N(2)–Re–O(2)	92.0(3)	O(2)–C(37)–C(38)	109.8(9)
P(2)–Re–N(2)	79.6(2)	Re–P(2)–C(7)	99.3(3)	O(1)–Re–O(2)	160.8(3)		
P(2)–Re–O(1)	88.8(2)	P(2)–C(7)–C(12)	113.0(7)				

(*c*) Complex **12**

Re–Cl	2.436(3)	P(1)–C(1)	1.81(1)	Re–N(1)	1.986(9)	P(2)–C(25)	1.81(1)
Re–P(1)	2.429(3)	P(1)–C(13)	1.82(1)	Re–N(2)	2.029(8)	P(2)–C(31)	1.82(1)
Re–P(2)	2.479(3)	P(1)–C(19)	1.82(1)	N(1)–C(6)	1.36(1)	N(2)–C(12)	1.38(1)
Re–O	1.767(7)	P(2)–C(7)	1.79(1)	C(1)–C(6)	1.42(1)	C(7)–C(12)	1.41(1)
O–Re–P(1)	94.9(2)	Re–P(1)–C(1)	99.6(4)	Cl–Re–N(2)	89.2(2)	C(1)–P(1)–C(13)	104.8(5)
O–Re–P(2)	87.3(2)	P(1)–C(1)–C(6)	113.3(8)	P(1)–Re–P(2)	98.2(1)	C(1)–P(1)–C(19)	105.7(5)
O–Re–Cl	96.7(2)	C(1)–C(6)–N(1)	120.6(1.0)	P(1)–Re–N(1)	80.4(3)	C(13)–P(1)–C(19)	108.4(5)
O–Re–N(1)	108.6(3)	C(6)–N(1)–Re	125.6(7)	P(1)–Re–N(2)	82.9(2)	C(7)–P(2)–C(25)	107.1(5)
O–Re–N(2)	162.8(3)	Re–P(2)–C(7)	102.3(3)	P(2)–Re–N(1)	164.1(3)	C(7)–P(2)–C(31)	108.0(4)
Cl–Re–P(1)	164.0(1)	P(2)–C(7)–C(12)	113.7(7)	P(2)–Re–N(2)	76.3(2)	C(25)–P(2)–C(31)	103.2(5)
Cl–Re–P(2)	93.4(1)	C(7)–C(12)–N(2)	118.0(8)	N(1)–Re–N(2)	87.9(3)		
Cl–Re–N(1)	85.4(3)	C(12)–N(2)–Re	129.7(7)				

(*d*) Complex **13**

Re–O	1.69(1)	Re–Cl	2.422(6)	P(1)–C(19)	1.82(2)	P(2)–C(7)	1.79(2)
Re–P(1)	2.434(5)	Re–P(2)	2.476(5)	P(2)–C(25)	1.83(2)	N(1)–C(6)	1.33(2)
Re–N(1)	2.01(1)	Re–N(2)	2.04(1)	N(2)–C(12)	1.39(2)	C(1)–C(6)	1.43(2)
P(1)–C(1)	1.82(2)	P(1)–C(13)	1.82(2)	C(7)–C(12)	1.41(2)		
O–Re–P(1)	93.2(5)	Re–P(1)–C(1)	99.9(6)	Cl–Re–N(2)	92.3(4)	C(1)–P(1)–C(13)	104.4(8)
O–Re–P(2)	89.5(5)	P(1)–C(1)–C(6)	113(1)	P(1)–Re–P(2)	99.5(2)	C(1)–P(1)–C(19)	106.5(8)
O–Re–Cl	97.5(5)	N(1)–C(6)–C(1)	122(1)	P(1)–Re–N(1)	80.2(5)	C(13)–P(1)–C(19)	104.8(8)
O–Re–N(1)	109.0(7)	Re–N(1)–C(6)	126(1)	P(1)–Re–N(2)	80.2(4)	C(7)–P(2)–C(25)	107.9(8)
O–Re–N(2)	162.7(6)	Re–P(2)–C(7)	102.6(6)	P(2)–Re–N(1)	161.4(5)	C(7)–P(2)–C(31)	109.9(8)
Cl–Re–P(1)	164.8(2)	P(2)–C(7)–C(12)	114(1)	P(2)–Re–N(2)	75.9(4)	C(25)–P(2)–C(31)	100.7(8)
Cl–Re–P(2)	91.3(2)	N(2)–C(12)–C(7)	117(1)	N(1)–Re–N(2)	85.8(6)		
Cl–Re–N(1)	86.2(5)	Re–N(2)–C(12)	130(1)				

monodentate coligand co-ordinated *trans* to the M=O linkage. They are all shifted upfield compared with those of the free ROH ligands. All 'equatorial' rhenium complexes show a single peak in the ^{31}P-{^{1}H} NMR spectra, consistent with two equivalent phosphorus atoms in the co-ordination sphere. Their chemical shifts range from δ 15.53 to 25.51 depending on the coligand *trans* to the [Re=O]$^{3+}$ core, the most upfield signal being that arising from the phosphorus co-ordinated to the complex having the *trans* butoxo group. Many attempts to record the ^{31}P NMR spectra of the technetium derivatives have been made, but no relevant peaks for co-ordinated diamagnetic species have been obtained, the only detectable signal falling at δ 41.05, characteristic of the oxidized HL ligand. Identical results were obtained by adding the corresponding ROH to the $CDCl_3$ solutions, in an attempt to support the sixth co-ordinating coligand.

Table 4 Infrared[a] (cm^{-1}) and NMR[b] spectral data

	IR		NMR			
Compound	ν(M=O)	ν(N–H)	^{31}P	N–^{1}H	^{1}H of OR chain	^{1}H aromatic
HL		3401, 3318	−14.94 (s)	4.09 (br s)		6.60–7.40
1 [TcOL$_2$(OMe)]	878	3303	n.d.	8.63 (s)	2.66 (t)	6.65–7.90
2 [TcOL$_2$(OEt)]	857	3294	n.d.	8.61 (s)	2.92 (m), 0.07 (t)	6.65–7.90
3 [ReOL$_2$(OH)][c]	920, 930	3305	16.75 (s)	9.07 (s)	−0.69 (s)	6.60–7.90
4 [ReOL$_2$(OMe)]	895	3298	16.22 (s)	8.96 (s)	2.74 (s)	6.65–7.90
5 [ReOL$_2$(OEt)]	887	3300	15.97 (s)	8.92 (s)	2.91 (m), 0.00 (t)	6.60–7.90
6 [ReOL$_2$(OPr)]	902	3301	15.61 (s)	8.94 (s)	2.82 (t), 0.36 (m), −0.03 (t)	6.65–7.90
7 [ReOL$_2$(OBu)]	897	3302	15.53 (s)	8.93 (s)		6.60–7.75
8 [ReOL$_2$(OC$_2$H$_4$OH)][d]	882	3299	18.62 (s)	9.06 (s)	2.89 (m), 2.53 (m)	6.65–7.85
9 [ReOL$_2$(OC$_3$H$_6$OH)][e]	913	3303	18.86 (s)	9.08 (s)	2.83 (d), 2.47 (m), 0.43 (d)	6.65–7.90
10 [ReOL$_2$(OPh)]	927	3301	20.55 (s)	9.20 (s)		6.60–7.85
11 [ReOL$_2$(O$_2$CMe)][f]	946	3292	25.51 (s)	9.38 (s)	1.29 (s)	6.70–7.85
12 α-[ReOL$_2$Cl][g]	899	3333, 3255	9.75 (d), 18.96 (d)	10.50 (s), 4.85 (d)		5.70–7.80
13 β-[ReOL$_2$Cl][h]	907	3335, 3341	9.21 (d), 19.78 (d)	10.50 (br s), 4.94 (d)		5.70–7.80
14 [ReOL$_2$Br]	906	3335	8.55 (d), 19.99 (d)	10.71 (s), 4.92 (d)		5.70–7.90
15 [ReOL$_2$I]	905	3331	6.46 (d), 19.46 (d)	10.89(s), 4.84 (d)		5.70–7.90

[a] As Nujol mulls for Tc and KBr pellets for Re. [b] Chemical shifts in ppm with multiplicities in parentheses. s = Singlet, d = doublet, t = triplet, m = multiplet, br = broad, n.d. = not detectable. [c] ν(O–H) 3599 (sh) cm^{-1}. [d] ν(O–H) 3505 (sh) cm^{-1}. [e] ν(O–H) 3545 (br) cm^{-1}. [f] ν(C=O) 1622 cm^{-1}. [g] ν(Re–Cl) 271 cm^{-1}. [h] ν(Re–Cl) 281 cm^{-1}.

Table 5 Relevant spectroscopic data for selected rhenium complexes

	IR (cm^{-1})			NMR			
Compound	ν(Re=O)	ν(N–H)$_{eq}$	ν(N–H)$_{ax}$	N–^{1}H$_{eq}$	N–^{1}H$_{ax}$	^{31}P	Re=O/Å
11 [ReOL$_2$(O$_2$CMe)]	946	3292	—	9.38	—	25.51	—
10 [ReOL$_2$(OPh)]	927	3301	—	9.20	—	20.55	—
5 [ReOL$_2$(OEt)]	887	3300	—	8.92	—	15.97	1.692
12 α-[ReOL$_2$Cl]	899	3255	3333	10.50	4.85	18.96, 9.75	1.69
13 β-[ReOL$_2$Cl]	907	—	3338	—	4.94	19.78, 9.21	1.767

'Twisted' rhenium complexes give two ^{31}P NMR signals consistent with two non-equivalent phosphorus atoms in the inner core, at δ 19.50 ± 0.50 and 8.00 ± 1.60 respectively, the latter being more shielded when traversing the halide series from Cl to I. In addition the proton spectra show a wider region for aromatic protons (from δ 5.70 to 7.90) than those of the 'equatorial' species, and two amido signals at δ 4.90 ± 0.06 and 10.70 ± 0.20.

Structural Commentary.—The identification of the atoms and the four molecular structures are shown in Figs. 1, 2, 4 and 5. All the structures contain discrete monomeric neutral complex units, there is no intermolecular bonding of significance and the co-ordination geometry about the metal is highly distorted octahedral. The structures of [TcOL$_2$(OMe)] **1** and [ReOL$_2$(OEt)] **5** are superimposable (Fig. 3), the weighted root mean square (r.m.s.) deviation, derived from the BMFIT program,[13] being only 0.025 Å, when the fitting is performed using the octahedron atoms; nevertheless, the two complexes differ significantly in the periphery. In **1** the O(1)–Tc–O(2) angle is only 158.3° (the corresponding value in **5** is 160.8°) and the 'bite' angles are 79.8 and 79.6° (78.7 and 79.6° in **5**). The geometry could be also described as distorted square pyramidal, a typical geometry for complexes containing either the Tc^{V}O or Re^{V}O core. Within this description the metal atoms are displaced from the mean plane of the P$_2$N$_2$ donor atom set (by 0.22 Å in **1** and 0.21 Å in **5**) towards the oxo-O(1) atom, the insertion of the methoxide (or ethoxide) group occurring *trans* to O(1). This geometry is different from that found in [TcO(OEt)Br$_2$(4O$_2$N-py)$_2$] (4O$_2$N-py = 4-nitropyridine)[14] in which the Tc atom is not substantially displaced from the equatorial plane. In the P$_2$N$_2$O$_2$ co-ordination polyhedron of **1** the Tc atom is 1.15 Å from the N(1), N(2), O(2) plane and −1.11 Å from the P(1), P(2), O(1) plane, the angle between the two triangular faces being 16.1°. The corresponding values for **5** are 1.17, −1.09 Å and 14.6°. Although each pair of bidentate PN ligand donor atoms is nearly coplanar with their benzene ring, the two PCCN rings in **1** and in **5** are bent away from the oxo-group, making dihedral angles of 24.6 and 10.1° in **1** (23.6 and 9.8° in **5**) with the P$_2$N$_2$ mean plane and 34.1° in **1** (33.0° in **5**) with each other. The resulting geometry assumes consequently a somewhat 'umbrella' arrangement. However, it is asymmetrical, since, whereas the Tc–P(2)–C(7)–C(8)–N(2) five-membered ring is roughly planar (torsion angles in the range −4.5 to 4.5° for **1** and −4.7 to 4.8° for **5**), the Tc–P(1)–C(1)–C(2)–N(1) ring is puckered (torsion angles in the range −14.8 to 17° in **1** and −16.9 to 14.2° in **5**). As seen in Fig. 1, the Tc–O(2)–CH$_3$ plane is nearly normal (dihedral angle 91.7°) to the equatorial mean plane (the corresponding value is 92.4° in **5**) and the only close approach of O(2) is at 2.30 Å with H–C(18) [2.33 Å with H–C(20) in **5**]. The angles between the M=O(1) bond and the equatorial nitrogen donors are remarkably different from 90° (105.8 and 103.6° in **1** and 104.6 and 102.6° in **5** respectively), while they are close to 90° with the phosphorus donor [Table 3(*a*) and (*b*)], and the angle between the normal to the P$_2$N$_2$ plane and the O(1) ··· O(2) line is 0.8° in **1** and 1.2° in **5**. The Tc–N(1) and Tc–N(2) distances [both 1.97(1) Å] are consistent with those found in the similar compound [Tc^{III}L$_2$(HL)]$^{+}$ [1] and [Tc(NHC$_6$H$_4$S)$_3$][15] and they confirm that both the bidentate ligands are monoanionic. All other distances and angles are in the expected range[16] and do not deserve any comment.

Also in the neutral 'twisted' [Re^{V}OL$_2$Cl] **12** the co-

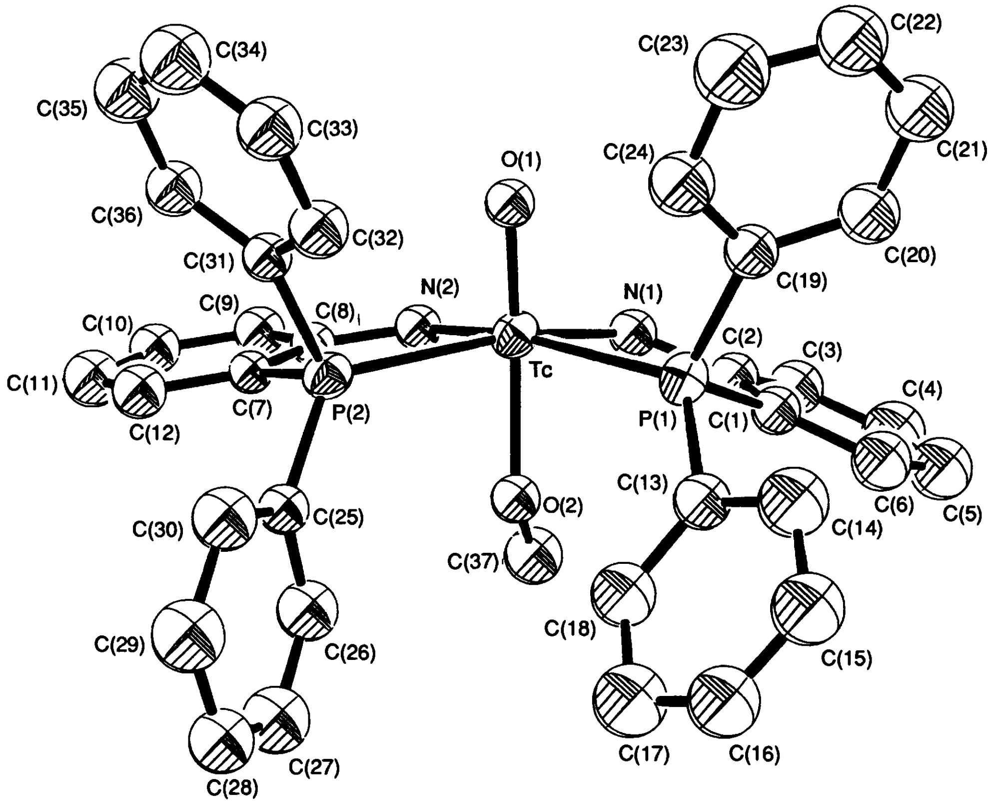


Fig. 1 An ORTEP view of complex 1, showing the atom labelling scheme; the thermal ellipsoids are drawn at 50% probability and hydrogen atoms are omitted for clarity

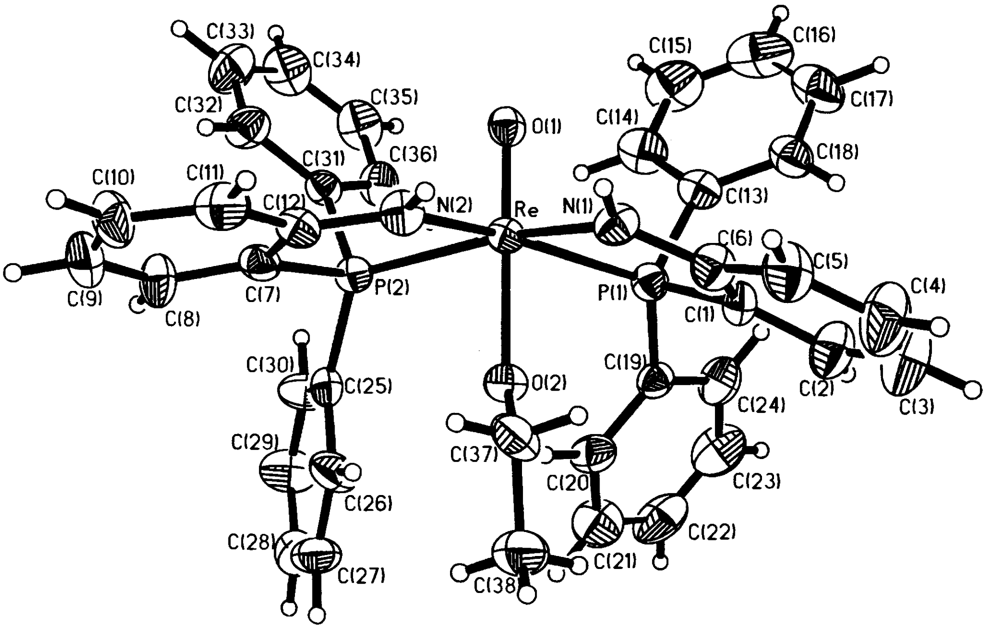


Fig. 2 An ORTEP diagram of complex 5 with atom contours shown at 50% probability

ordination around the metal is approximately octahedral with the two monoanionic ligands mutually orthogonal, one ligand bridging an equatorial and an apical position and the other two equatorial positions. The equatorial plane is completed by the Cl atom and the remaining position is occupied by the O(oxo) atom. Complex **13** represents a different crystalline form of **12**. Their molecular structures are essentially identical, the two modifications showing normal distances and the major difference residing in the relative orientation of the C(31)–C(36) phenyl group at P(2), as in Fig. 6. The P(1), N(1), P(2), Cl atoms define an 'equatorial' plane with the Re atom pushed upwards by 0.25 Å in **12** and 0.27 Å in **13**, towards the oxo atom. The 'inner core' is distorted from an ideal octahedral configuration mainly by this movement such that the angles Cl–Re–P(1) and N(1)–Re–P(2) are 164.0 and 164.1°, respectively (164.8 and 161.4° in **13**); the O(oxo)–Re–N(2) angle is significantly non-linear at 162.8° (162.7° in **13**) and the bond angles in the equatorial plane are rather far from 90°. The equatorial bidentate ligand shows a P(1) ••• N(1) distance of 2.87 Å (2.88 Å in **13**) with a 'bite' angle of 80.4° (80.2° in **13**), while in the ligand bridging an equatorial and an apical position [P(2) $\cdots$ N(2) of 2.80 Å in both **12** and **13**] the angle is reduced to 76.3° (75.9° in **13**), the two quite planar ligands being almost mutually orthogonal (94.6 and 102.4° in **12** and **13**, respectively). Most of the bond lengths show no unusual features, being within the range expected from comparison of 21 other six-coordinate monooxo complexes of Re^V (ref. 17 see Table 5, refs. 17–20). Nevertheless, it is of interest to point out three results: (*i*) in **12** the Re=O distance of 1.767(7) Å is considerably longer than those found in the literature (1.65–1.73 Å) and the reason for this is obscure, from the 'crystal structure point of view', not easily attributable to any inter- or intra-molecular interaction [shortest contact 2.46 Å with the H atom at C(32)]; on the contrary, the Re=O distance in **13** is as expected (1.685 Å); (*ii*) the Re–N distances [1.986(9) and 2.029(8) Å in **12** and 2.01(1) and 2.04(1) in **13**] are shorter than those reported (2.09–2.26 Å), but the situation parallels that found in [*N,N′*-3-azapentane-1,5-diylbis(salicylideneiminato)(3 –)-*N,N′,N″,O,O′*]oxorhenium(v),[18] in which the Re–N(imine) distances are of 2.04 and 2.06 Å, while the third distance, between Re and the N atom in planar geometry, of only 1.91 Å is diagnostic for p_π–d_π electron donation from the ligand to rhenium, as confirmed by the value of 1.93 Å in the binuclear complex $[ReO\{2\text{-}[OC_6H_4\text{-}2\text{-}CH_2N(CH_2)_2S(CH_2)_2NHCH_2]C_6H_4O\}_2ReO]$[19] for the Re–N($sp^2$) bond length; (*iii*) the Re–N(2) bond, *trans* to the oxo ligand, is the longest [2.029(8) Å in **12** and 2.04(1) Å in **13**], presumably as a result of some *trans* influence of the multiply bonded oxo group, and this effect is not so dramatic as found, for example, in monooxorhenium(v) octahedral complexes containing the hydrotris(pyrazolyl)borate ligand.[20]

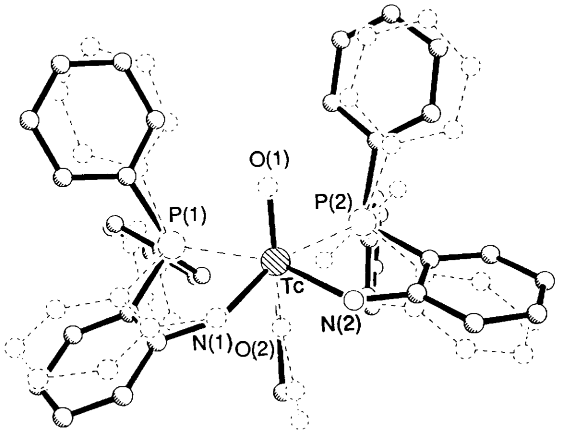


Fig. 3 Superimposition of structures **1** and **5** (– – – –)

Discussion

Technetium Complexes.—The reaction of the alcohol-soluble $[NBu_4][TcO_4]$ with the ligand HL, in rigorously controlled stoichiometry, leads to the formation of oxotechnetium(v) complexes. The correct amount of the ligand and the temperature permits control of the oxidation state of the resulting complexes. One molecule of the ligand, through the formation of the phosphine oxide, contributes to extract one oxygen from the pertechnetate anion,[11] which is simultaneously reduced to Tc^V, while the remaining two oxygens may undergo ligand-exchange reaction with two further molecules of HL. However, since the yields of the reactions are both close to 60% and the ^1H and ^{31}P NMR spectra are somewhat invalidated by the presence of a paramagnetic species, part of the pertechnetate ends up as the complex $[Tc^{III}L_3]$.[1]

Literature data show that either diamino (only σ-donor) or diphosphino (σ-donor π-acceptor) ligands always give dioxotechnetium(v) complexes.[2,3] Generally, the reaction mechanism involves co-ordination of H_2O *trans* to an oxo-group[21] which, after a first deprotonation, produces the intermediate *trans*-hydroxo complex which undergoes a second deprotonation yielding the dioxo species. Many attempts to obtain the dioxo species were made, for instance by performing reaction (1) in MeCN with the presence of water or upon standing the reaction mixture in air, as well as by exposing $[TcOL_2(OR)]$ solutions to air. Dark oily compounds were always obtained the IR spectra of which showed unambiguously the intense band of pertechnetate at 900 cm^{-1}. Even the complex $[TcOL_2(OH)]$ was never isolated, indicating that, either in MeOH or EtOH solutions, the respective $[TcOL_2(OR)]$ complexes are thermodynamically favoured.

The ligand HL acts, in the present complexes, as a mixed π-acceptor(P)–π-donor(N) ligand and, consequently, its

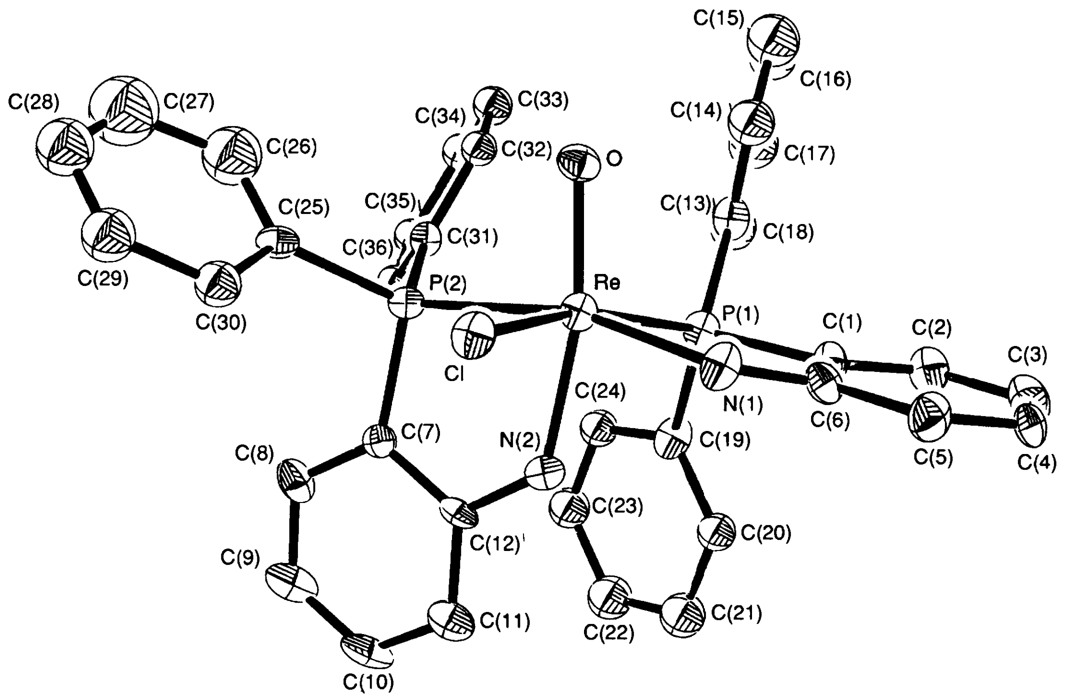


Fig. 4 An ORTEP view of complex **12**. Hydrogen atoms have been omitted for clarity

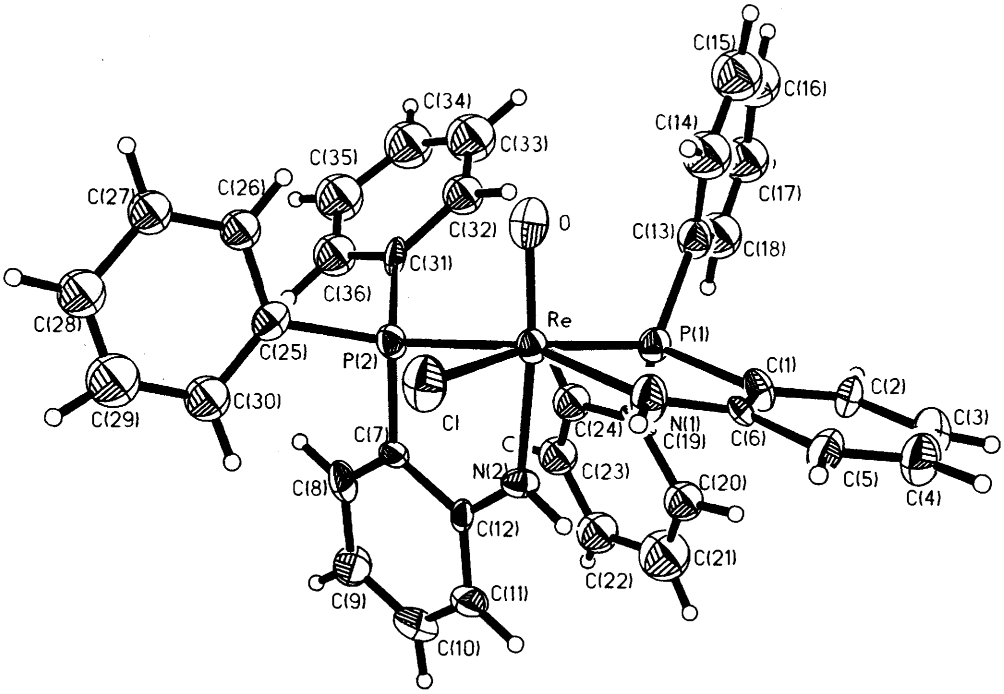


Fig. 5 An ORTEP view of complex **13**

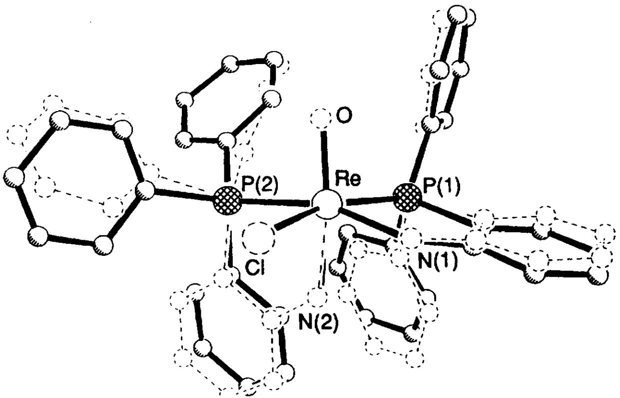


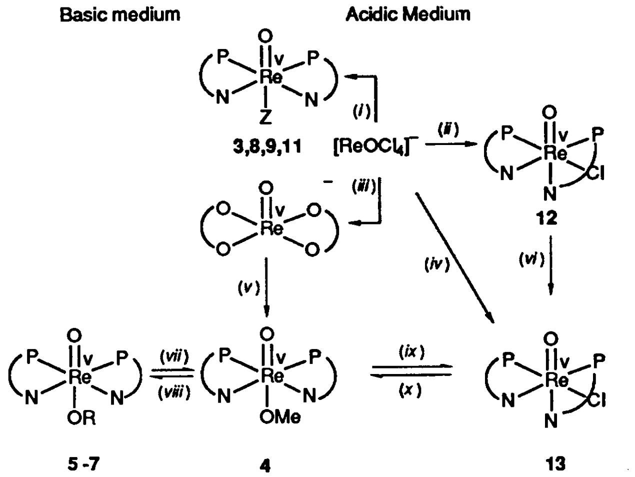
Fig. 6 Superimposition of structures **13** and **12** (– – – –)

behaviour is somewhat in between that of bis(diphosphine) and bis(diamine) ligands. Moreover, upon co-ordination, the aniline group is always deprotonated. The peculiar *cis*-P 'equatorial' co-ordination of two phosphinoamido ligands allows the best delocalization and balance of the negative charge density through both *trans* N–P inter-ligand and *cis* N–P intra-ligand, π-donor–π-acceptor systems of the co-ordinating atom sets. In addition, such a configuration, together with the strong acid character of the $[Tc{=}O]^{3+}$ core, favours the co-ordination of a further group *trans* to the oxo core. In this way an alcohol readily co-ordinates and, in order to compensate the positive charge of the resulting complex, it deprotonates, forming the alcoholate which, acting as a strong donor, contributes to diminish the oxo *trans*-labilizing effect.[21] Nevertheless, the alcoholate is kept at the unusual distance of 2.00 Å from the Tc atom. A combination of several factors is therefore responsible for the remarkable weakening of the Tc=O bond, as demonstrated by the long values of the Tc=O bond distances accompanied by very low values of the Tc=O stretches in the IR spectra. The ν(Tc=O) value is at 878 cm^{-1} for the methoxo derivative and 857 cm^{-1} for the ethoxo one, indicating a stronger Tc–OEt bond with respect to Tc–OMe, in agreement with the higher basicity of OEt due to the greater $+I$ effect of the ethyl group. The unusual value of 857 cm^{-1} for a ν(Tc=O), much beyond the low-energy end of the range thus far observed for monooxotechnetium(v) complexes (910–1020 cm^{-1}) and tailing into the region characteristic of *trans*-dioxo asymmetrical stretching (750–850 cm^{-1}),[3–5] is consequently due to the presence of both the *trans* oxo-alcoholate group and mainly to the amido groups in the equatorial plane. The lengthening of any Tc–O bond distances is expected when one or two N-amido nitrogens co-ordinate to the metal.[22,23]

Although the $[TcOL_2(OMe)]$ and $[TcOL_2(OEt)]$ complexes are interconvertible, which would imply a relative lability of the coligand *trans* to Tc=O, no other alcoholate (as for rhenium analogues) or negatively charged ligand (as halide) were found co-ordinated in that position. On the other hand, treating $[NBu_4][Tc^{V}OCl_4]$ with two HL ligands leads to lower-oxidation-state products, thus the *trans*-non-co-ordination of the chloride in the $[Tc^{V}OL_2]^+$ system can be explained in terms of its lower basicity with respect to that of both $^-$OMe and $^-$OEt. In addition, the steric hindrance does not allow the co-ordination of bulkier alcohols *trans* to the $[Tc{=}O]^{3+}$ core.

Rhenium Complexes.—The ligand HL reacts with a pre-reduced oxorhenium(v) starting material and produces, *via* ligand-exchange reaction, complexes the structure of which depends on the pH of the reaction medium. In all the reactions the original oxidation state Re^{V}, along with the Re=O moiety, is always preserved. Only in the presence of a relatively strong acid, like CF_3CO_2H, which increases the reducing power of the phosphine ligand, an excess of HL can produce a reduced rhenium complex. According to Scheme 1 two routes of preparation are distinguishable; each one identifies a series of compounds.

(*a*) *The 'equatorial' series* $[ReOL_2(OR)]$. 'Equatorial' $[ReOL_2(OR)]$ complexes are prepared in basic media, either NaO_2CMe or NEt_3. Their main feature is the co-ordination of two deprotonated ligands with the phosphorus in *cis* mutual position in the equatorial plane (orthogonal to the Re=O linkage); the OR coligand saturates the apical position, *trans* to the Re=O moiety. The stability of these rhenium complexes is higher than that of the analogous technetium compounds, thus allowing a complete chemico-physical characterization even though the alkoxo coligand is easily exchangeable. This



Scheme 1 (*i*) MeCN, $\mathrm{NEt_3}$, HZ, 2HL; (*ii*) 2HL, MeOH; (*iii*) MeOH, $\mathrm{NaO_2CMe}$, $\mathrm{eg^-}$; (*iv*) 2HL, EtOH or MeCN; (*v*) 2HL; (*vi*) $\mathrm{H^+}$ (catalyst); (*vii*) MeOH; (*viii*) ROH; (*ix*) HCl, MeOH or MeCN; (*x*) $\mathrm{NEt_3}$, MeOH

property is exploited to prepare all the other derivatives by simple dissolution in $\mathrm{CH_2Cl_2}$ (*i.e.* of the methoxo derivative) and addition of the new R′OH ligand, according to equation (3).

$$[\mathrm{ReOL_2(OR)}] \underset{\mathrm{ROH}}{\overset{\mathrm{R'OH}}{\rightleftharpoons}} [\mathrm{ReOL_2(OR')}] \qquad (3)$$

An incoming primary alcohol, favoured by the mass effect, replaces the originally co-ordinated alkoxo group and forms a new six-co-ordinated stable 'equatorial' species. On the contrary, the exchange reaction of branched alcohols (*i.e.* $\mathrm{Pr^iOH}$ or $\mathrm{Bu^tOH}$), even though strongly supported by the need of the $[\mathrm{Re^VOL_2}]^+$ species to disperse the positive charge, leads to colourless solutions containing perrhenate, the bulkiness of the incoming alcoholate overcoming any electronic effect. In addition, when non-alcoholic solvents such as non-anhydrous MeCN or $\mathrm{Me_2CO}$ are added to a $\mathrm{CH_2Cl_2}$ solution of an alkoxo prototype complex only mixtures are obtained, the hydroxo derivative $[\mathrm{ReOL_2(OH)}]$ being the main product.

The Re=O stretches in the IR spectra of 'equatorial' alcoholate compounds do not follow a general trend along the series, however the values of the methoxo, propoxo and butoxo derivatives are included in the narrow range 895–902 $\mathrm{cm^{-1}}$. The ethoxo derivative, as found for Tc, has the lowest value at 887 $\mathrm{cm^{-1}}$ because of the higher nucleophilicity of the ethoxo group with respect to the methoxide. All the 'equatorial' glycolate complexes are monomeric species, showing, in the infrared spectra the band of the free OH stretch. The value of 882 $\mathrm{cm^{-1}}$ for the ν(Re=O) of the ethylene glycolate complex is the lowest of the 'equatorial' series. The glycolate and the ethoxo complexes are, among the 'equatorials', the derivatives which better satisfy the charge requirement of the $[\mathrm{Re^VOL_2}]^+$ system.

Significant is the behaviour of the acetate complex **11** which exhibits at 946 $\mathrm{cm^{-1}}$ the highest Re=O stretching of the series. Acetate is a weaker base than any other alcoholate considered herein, therefore it is most likely to satisfy the charge requirement of the complex. In spite of this it still co-ordinates *trans* to the Re=O, but the weakness of the $\mathrm{Re{-}O_2CMe}$ bond gives rise to a stronger Re=O bond. Last, but peculiar to rhenium, is the possibility to obtain the hydroxo derivative the IR spectrum of which shows two Re=O stretching vibrations at 930 and 920 $\mathrm{cm^{-1}}$; whether this is due to a solid-state effect or to different isomers (see below) is difficult to ascertain, since the ^{31}P NMR spectrum shows unequivocally only one peak in solution. In the IR spectrum a sharp ν(O–H) at 3599 $\mathrm{cm^{-1}}$ indicates a strong O–H bond due to the electronic drainage of the Re=O group. As reported for Tc it was not possible to isolate any dioxorhenium(v) derivative, although starting from $[\mathrm{ReO_2(py)_4}]^+$. Again the reason for this behaviour resides in the low acidity of the $[\mathrm{O{=}Re{-}OH}]^+$ core, well described by the values of ν(O–H) and by the chemical shift of O^{1}H falling at δ −0.69, which by deprotonation would lead to formation of the dioxo core. In addition, as previously found for analogous technetium complexes, it was not possible to obtain the 'equatorial' *trans* oxochloro derivative, because of the low basicity of the chloride ligand with respect to alkoxides; the 'twisted' complex is always produced.

(*b*) *The 'twisted' series* $[\mathrm{ReOL_2X}]$. 'Twisted' complexes are prepared either starting from $[\mathrm{NBu_4}][\mathrm{ReOCl_4}]$ or from any 'equatorial' $[\mathrm{ReOL_2(OR)}]$ complex in acid media. They contain two virtually orthogonal co-ordinated $\mathrm{L^-}$ ligands, one in the equatorial plane, while the second is bonded keeping the phosphorus still in the plane *cis* to that of the other ligand, but with the amido nitrogen *trans* to the Re=O moiety. Six-co-ordination and neutrality are achieved by a halide ion in the remaining equatorial site. When a halide is forced to co-ordinate, both by the acid medium and its excess, its lower basicity, with respect to the amido group, always prevents co-ordination *trans* to Re=O; even the presence of an alcohol, which can compete with the halide only if it can be deprotonated, does not affect the result.

The IR spectra of all 'twisted' species show slightly different Re=O stretches in the range 905 (iodide)–907 (chloride) $\mathrm{cm^{-1}}$, indicating the lack of influence of the halide in determining variations in the electron density of the $[\mathrm{Re{=}O}]^{3+}$ core. The complex $[\mathrm{ReOL_2Cl}]$ exists in two isomeric forms (herein called α and β): α is produced only starting from $[\mathrm{NBu_4}][\mathrm{ReOCl_4}]$ in MeOH solvent, while β is prepared (*i*) starting from $[\mathrm{NBu_4}][\mathrm{ReOCl_4}]$ in solvents other than MeOH, (*ii*) in protic or non-protic solvents from any 'equatorial' compound by adding HCl, and (*iii*) from the α derivative by adding HCl. Both α and β forms regenerate any 'equatorial' complex in basic ROH.

Electronic Spectra.—The complex $[\mathrm{TcOL_2(OMe)}]$ exhibits in its UV/VIS spectra three bands at 515 (a), 415 (b) and 350 (c) nm, while the homologous $[\mathrm{TcOL_2(OEt)}]$ shows only two bands at 485 and 335 nm, at higher energy, but somewhat with the trend of a and c of the methoxo derivative. Totally absent is the band b around 415 nm. Rhenium 'equatorial' analogues possess spectra with only two bands at 395 and 320 nm. On the other hand, the complex $[\mathrm{TcL_2Cl_2}]$, partially characterized by mass spectroscopy (see above), shows in its UV/VIS spectrum (in $\mathrm{CH_2Cl_2}$) only a charge-transfer band at 405 nm. Thus, the band at 415 nm, present in the spectrum of $[\mathrm{TcOL_2(OMe)}]$, could be explained by invoking the transformation of a portion of the 'equatorial' methoxo derivative into the reduced chlorinated species.

'Equatorial' complexes of Re differ from those of Tc since their UV/VIS spectra are identical for all derivatives, as a consequence of the higher lability of the site *trans* to Re=O with respect to that *trans* to Tc=O. Since water is present, as impurity, in all solvents, the 'equatorial' rhenium complexes can easily exchange $^-$OR with $^-$OH; in solution the $[\mathrm{ReOL_2(OH)}]$ complex is the only one present, being the most stable species of the series. Confirmation of this comes, for instance, from the NMR spectrum in $\mathrm{CDCl_3}$ of the complex $[\mathrm{ReOL_2(OEt)}]$, where it is possible to follow the time release of free ethanol and the simultaneous growth of the signals related to both the N–^{1}H and O–^{1}H of the hydroxo derivative.

It is difficult to attribute correctly both the charge-transfer (c.t.) bands for the equatorial complexes since phosphino as well as amido ligands are reported to have c.t. bands in the region 250–350 nm.[22a,24] 'Twisted' rhenium complexes show four bands; that ranging from 450 to 480 nm, the most sensitive to halide variation, could therefore be attributed to the halogen-to-rhenium c.t. transition. Along the series, this band is of lowest energy for the iodide derivative since $\mathrm{I^-}$ is a better reductant than $\mathrm{Br^-}$ and $\mathrm{Cl^-}$.[24]

NMR Spectra.—The analysis of ^{1}H and ^{31}P NMR spectra of

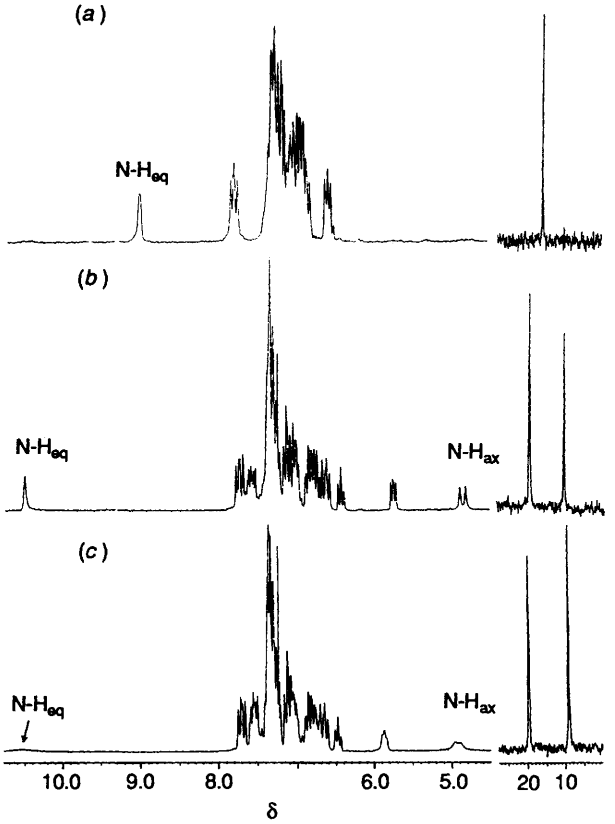
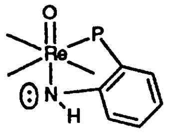


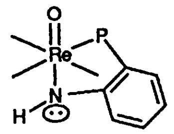
Fig. 7 Representative proton and ^{31}P NMR spectra of 'equatorial' **3** (*a*) and 'twisted' **12** (*b*) and **13** (*c*) rhenium complexes

both 'equatorial' and 'twisted' complexes confirms that their structures in solution are identical to those found in the solid state. A representative example of both proton and phosphorus NMR spectra for an 'equatorial' and 'twisted' rhenium complex is shown in Fig. 7.

'Equatorial' species possess a symmetry plane and, therefore, show only one phosphorus and one N-amido proton signal, in agreement with the equivalent equatorial co-ordination of two L^- chelates. The alcoholato group co-ordinated *trans* to the oxo moiety shows its typical proton signals arising from the alkyl chain, markedly shifted upfield with respect to those of the free alcohol. On the contrary, the aromatic protons of the equatorially co-ordinated L^- ligand are, on average, shifted downfield. The last two observations indicate how the excess of negative charge density located on the Re=O moiety needs to be delocalized through the coligand *trans* to the Re=O, and how the acid character of a high-valence d^2 system needs to be balanced by the equatorially co-ordinated L^- ligands. The Re=O stretching vibration represents a very sensitive probe for determining the acidity and basicity of the oxo core as a function of the ancillary ligands. A low value is diagnostic of a partial donation from the oxo to other groups, thus the weakening of the Re=O multiple bond is associated with relatively stronger co-ordinated *trans* and *cis* ligands. Traversing the *trans* to Re=O coligand series in 'equatorial' species from ethoxo to phenoxo and acetato, the shortening of the Re=O bond distance, is accompanied by an ipsochromic shift from 887 to 946 cm^{-1} in the infrared and a downfield shift of both amido protons (from δ 8.92 to 9.38) and phosphorus (from δ 15.97 to 25.51) in the NMR spectra.

'Twisted' rhenium species possess neither symmetry plane nor symmetry axis and therefore they show more complicated NMR patterns. Each complex exhibits two phosphorus signals arising from two asymmetrically co-ordinated phosphinoamido ligands. The associated $^3J_{PP}$ coupling constant (average 6.4 Hz) is consistent with a *cis*-P configuration and therefore the structure is described according to Figs. 5 and 7. The replacement of a co-ordinated chloride with a bromide or an iodide ligand produces an appreciable shift only on the more shielded phosphorus signal which is therefore attributed to the phosphorus *trans* to the halide. Proton spectra of all the 'twisted' species exhibit two main features: (*i*) aromatic proton signals occur from δ 5.70 to 7.80, the most upfield being those belonging to the phenyl ring in between the P and N of the twisted ligand; (*ii*) N-amido protons show two distinct signals, a downfield singlet for the equatorially co-ordinated one and an upfield doublet arising from that co-ordinated *trans* to the Re=O moiety. No homo- or hetero-coupling can be claimed to explain such a multiplicity, thus the appearance of the doublet can be interpreted only by assuming two orientations for the axial amido protons. Indeed, the partially sp^3-hybridized amido nitrogen becomes a chiral centre upon co-ordination, having four different substituents and, consequently, the amido proton may reside in two slightly different chemical environments giving two singlets of equal integration at very similar chemical shifts.





All the protons of the anilido ring *trans* to the Re=O group experience an upfield shift, as well as those of the alcoholate in the 'equatorial' series, because of the delocalization through the metal of the negative charge density of the oxo moiety. On the contrary, the equatorial N-amido proton of all 'twisted' species exhibits a singlet [sharp or broad depending on the crystalline form (see below)] at lower field with respect to the aromatic L^- protons, resembling the behaviour of related N-amido protons of the 'equatorial' type compounds.

α- and β-[ReOL$_2$Cl] *'Twisted' Complexes.*—Following different synthetic routes (see above) two 'twisted' [ReOL$_2$Cl] complexes have been obtained and structurally characterized in two different crystalline forms (α and β). The two forms are retained in solution showing similar, but not identical, spectroscopic parameters (see Table 4 and Fig. 7). In particular, the amido proton of the equatorial ligand gives a sharp singlet at δ 10.50 for the α form, but the corresponding signal for the β form is almost broadened into the baseline, at the same value and with the correct integration. Both forms show the upfield 'pseudo' doublet for the axial amido proton *trans* to the oxo core in the usual range. Similarly, the IR spectra show two well separated N–H stretches at 3333 and 3255 cm^{-1} for the α form and only one poorly resolved peak centred at 3338 cm^{-1} for the β form. As detailed in Table 5, spectroscopic evidence shows that ν(Re=O) of the α form is slightly bathochromically shifted (899 cm^{-1}) with respect to that of the β form (907 cm^{-1}). This difference is dramatically enhanced in the structural analysis where the Re=O bond distance is 1.767 Å for the α and 1.69 Å for the β form. The latter value falls within the range observed for 'equatorial' rhenium species while the former is surprisingly long. As evidenced for axial amido nitrogens, also 'equatorial' amido nitrogens become chiral centres upon co-ordination, opening the possibility for isomer formation. Hence, one might invoke a dipolar contact between the oxo-oxygen and the equatorial N-amido proton in the α form. This contact is responsible for the weakening of the Re=O multiple bond, and the intramolecular hydrogen bond contributes to stabilize such a configuration. There are no dipolar contacts in the β form, suggesting that the 'equatorial' amido proton is bonded on the opposite side to the Re=O moiety. This behaviour somewhat parallels that found by different authors[25] in oxometal(v) (M = Tc or Re) compounds with *N*-alkyl-substituted 1,2-(mercaptoacetamido)ethane ligands and reported as that of *anti* and *syn* epimers.

Conclusions

Neutral oxometal(v) complexes of the type $[MOL_2(OR)]$ (M = Tc or Re; R = alcoholate, glycolate or acetate), termed 'equatorial', have been synthesised by treating HL with $[TcO_4]^-$ (reduction–substitution route) or $[ReOCl_4]^-$ (ligand-exchange route) in basic media and strictly controlled metal/ligand stoichiometric ratio (1/3 for Tc, 1/2 for Re). By treating $[MOL_2(OR)]$ solutions with co-ordinating hydrohalogenic acid further reduction to lower-oxidation-state species occurs when M = Tc, while new stable and neutral oxorhenium(v) complexes of the type $[ReOL_2X]$ (X = Cl, Br or I), termed 'twisted', have been produced. 'Equatorial' complexes are characterized by the symmetric co-ordination (mutual *cis*-P configuration) of two bidentate L^- ligands in the equatorial plane orthogonal to the $[O{=}M{-}OR]^{2+}$ moiety. On the contrary, two mutual orthogonal L^- chelates are co-ordinated to rhenium (still *cis*-P positioned) in the 'twisted' derivatives, one ligand bridging an equatorial (P) and the apical site (N) *trans* to the Re=O linkage. The configuration of all reported bis(phosphinoamido)oxometal(v) complexes is highly dependent, apart from the phosphorus-based ligands, on the nucleophilicity of the ancillary coligand. The stronger nucleophile available in the reaction mixture always co-ordinates *trans* to the oxo group following the trend $^-OR > {}^-L(N_{amido}) > {}^-X > HOR$. Consequently, in basic media ^-OR ligands co-ordinate *trans* to the oxo moiety, giving 'equatorial' type complexes. By acidification with co-ordinating HX (X = halide), the ^-OR ligand is no longer deprotonated allowing an amido nitrogen, of an already co-ordinated L^- ligand, through a simple 90° twist, to saturate the free *trans* to Re=O site giving 'twisted' type complexes (the 'isomerization' produces unstable species which undergo further reduction when Tc is employed). Species X^- saturates the empty equatorial site and completes the six-co-ordination.

Both 'equatorial' and 'twisted' complexes exhibit very low M=O stretching vibrations in the infrared spectra [ν(Tc=O) ranges from 857 to 878 cm^{-1}, ν(Re=O) from 882 to 946 cm^{-1}], values somewhat in between the ranges usually observed for six-co-ordinated mono- and di-oxo species, respectively, of Tc and Re. Such behaviour, along with the rather long M=O bond distances exhibited by representative derivatives, indicates a partial reduction of the multiple-bond character of the M=O linkage. The origin of this lengthening is also the combination of the *trans* oxo co-ordination (favoured by a good M–L d_π–p_π orbital overlap) and the effective π-acceptor ability of the arylphosphines co-ordinated in the equatorial plane. The delocalization of the negative charge density from the oxo group to its *trans* co-ordinated ligand is well established, in the NMR spectra, by the consistent upfield shift exhibited by all the protons close to the co-ordinated atoms (O or N) *trans* to M=O.

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